

Podovik, A.N.

✓ New method of synthesis of esters of phosphonic and  
thiophosphonic acids. XXI. Addition of dialkyl thiophos-  
phites and dialkyl dithiophosphoric acids to anils. A. N.  
Podovik and M. K. Sergeeva (State Univ., Kazan). *Zh. Obshch.  
Khim.* 25, 1759-60 (1955); *J. C.A.* 41, 2687a;

50, 4808c.—An equimolar mixt. of  $(RO)_2PSH$  and the de-  
sired anil in a small vol. of EtOH was treated with a few  
drops of RONA soln.; almost no heat effect was observed.  
After 20-30 min. on a steam bath the mixt. was allowed to  
solidify. In reactions with  $(RO)_2PS_2H$ , this was added drop-  
wise to an equimolar amt. of anil in EtOH with ice cooling  
and the mixt. was finally heated 10-15 min. on a steam bath.  
The following  $RNHCH(R')P(S)(OR)_2$  were prepd. (R, R',  
R<sup>1</sup>, % yield, and m.p. given): *p*-MeOC<sub>6</sub>H<sub>4</sub>, Ph, Et, 43.2,  
48°, Ph, *p*-MeNC<sub>6</sub>H<sub>4</sub>, Et, 60, 100-100.5°, *p*-MeC<sub>6</sub>H<sub>4</sub>, Ph,  
Et, 62.3, 87°, *m*-MeC<sub>6</sub>H<sub>4</sub>, Ph, Et, 62.2, 77-8°, *m*-MeC<sub>6</sub>H<sub>4</sub>,  
*m*-MeC<sub>6</sub>H<sub>4</sub>, Et, 50, 84-5°, 1-C<sub>6</sub>H<sub>5</sub>, Ph, Et, 64.1, 138.5°,  
Ph, Ph, Bu, 78.3, 53°, *p*-MeOC<sub>6</sub>H<sub>4</sub>, Ph, Bu, 63.2, 45-8°,  
Ph, *p*-MeNC<sub>6</sub>H<sub>4</sub>, Bu, 81.2, 80°, *m*-MeC<sub>6</sub>H<sub>4</sub>, *m*-MeC<sub>6</sub>H<sub>4</sub>, 73,  
57-8°, Ph, *p*-MeC<sub>6</sub>H<sub>4</sub>, Bu, 61.3, 38°, *p*-MeC<sub>6</sub>H<sub>4</sub>, Ph, Bu,  
71.8, 75.5°, and *m*-MeC<sub>6</sub>H<sub>4</sub>, Ph, Bu, 65.8, 47-7.5°. The  
following  $RNHCH(R')SP(S)(OR)_2$  were prepd. from  $(R')_2O$ -  
PS<sub>2</sub>H (const. as above): Ph, Ph, Et, 69.1, 103-4°, *p*-Me-  
C<sub>6</sub>H<sub>4</sub>, Ph, Et, 60.4, 101-2°, *m*-MeC<sub>6</sub>H<sub>4</sub>, *p*-MeNC<sub>6</sub>H<sub>4</sub>, Et,  
93.5, 128-30°, *p*-MeC<sub>6</sub>H<sub>4</sub>, *p*-MeNC<sub>6</sub>H<sub>4</sub>, Et, 95.1, 145°,  
*p*-MeC<sub>6</sub>H<sub>4</sub>, *p*-MeCHC<sub>6</sub>H<sub>4</sub>, Et, 57.8, 110-11°, *p*-MeOC<sub>6</sub>H<sub>4</sub>,  
*p*-MeC<sub>6</sub>H<sub>4</sub>, Et, 88.5, 127-8°, and Ph, *p*-MeNC<sub>6</sub>H<sub>4</sub>, Me,  
28.9, 127°. Addn. of 4 g.  $(EtO)_2PS_2H$  to 2.29 g. BzH gave  
a slight rise in temp. augmented by addn. of a little EtONa-  
EtOH; after 15 min. on a steam bath followed by 1 day at

room temp. there was obtained 1 g. solid, presumably  $(EtO)_2$ -  
 $P(S)SCH(OH)Ph$ , m. 104°. *p*-ClC<sub>6</sub>H<sub>4</sub>N:CHPh with  
 $(EtO)_2PS_2H$  in Et<sub>2</sub>O gave a solid, m. 119-20°, identified as  
*p*-ClC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>HS<sub>2</sub>P(OEt)<sub>2</sub>, which apparently formed by hy-  
drolysis of the anil in contact with moisture. The salt  
was readily prepd. from the 2 components on mixing; simi-  
larly were prepd. the following salts: *PhNH\_2*HS<sub>2</sub>P(OEt)<sub>2</sub>,  
m. 80°, *p*-MeC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>HS<sub>2</sub>P(OEt)<sub>2</sub>, m. 87-8°, and 2-Cl-  
H<sub>2</sub>NH<sub>2</sub>HS<sub>2</sub>P(OEt)<sub>2</sub>, m. 118-17°. Since the anils were so  
readily attacked by moisture, the following technique was  
used for prepn. of the dithiophosphoric esters from the  
chloro. derivs.: 2.07 g. *p*-ClC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> in dry MePh was  
treated with 1.75 g. BzH, the mixt. heated briefly on a steam  
bath without access to atm. moisture, and the solvent re-  
moved *in vacuo*; the residual anil was treated with 3 g.  
 $(EtO)_2PS_2H$ , and the mixt. stirred a few min. and allowed  
to crystallize in an open dish, yielding 6.3 g. *p*-ClC<sub>6</sub>H<sub>4</sub>-  
NHCH(Ph)SP(S)(OEt)<sub>2</sub>, m. 96-7°. Similarly was prepd.  
90% *p*-ClC<sub>6</sub>H<sub>4</sub>NHCH(C<sub>6</sub>H<sub>4</sub>Me-*p*)SP(S)(OEt)<sub>2</sub>, m. 96°. Although a reaction evidently took place between  $(EtO)_2$ -  
PS<sub>2</sub>H and *p*-MeC<sub>6</sub>H<sub>4</sub>CHO or *p*-MeCHC<sub>6</sub>H<sub>4</sub>CHO in the  
presence or absence of NaOR, no cryst. products could be  
isolated.

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Pudovik, A.N.

New method of synthesis of esters of phosphonic and  
thiophosphonic acids. XXIII. Addition of phosphono-  
acetic ester, phosphonoacetone and its homologs to un-  
saturated compounds. A. N. Pudovik and N. M.  
Lebedeva. *J. Gen. Chem.* ~~U.S.S.R.~~ 25, 1803-6 (1955).  
(Engl. translation).—See *C.A.* 50, 8442c. B. M. R.

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New method of synthesis of esters of phosphonic and thiophosphonic acids. XXIII. Addition of phosphonoacetic ester, phosphonoacetone, and its homologs to unsaturated compounds. A. N. Pudovik and N. M. Lebedeva (Kavala Branch Acad. Sci. USSR). *Zhur. Obshchei Khim.* 25, 1920-1 (1955); cf. C. 4. 43, 5844; 56, 7073i. To the Na deriv. prep'd. from 1.70 g. Na and 15 g.  $\text{AcCH}_2\text{P(O)(OEt)}$  was added 13 g. MeI in  $\text{Et}_2\text{O}$ . After refluxing 5 hrs. there was obtained 11.6 g.  $\text{AcCHMeP(O)(OEt)}$ , b. 109-11°,  $n_D^{20}$  1.4335,  $d_4^{20}$  1.084. Similarly, 3.91 g. K, 19.6 g.  $\text{AcCH}_2\text{P(O)(OEt)}$ , and 15.6 g. EtI gave 14.8 g.  $\text{AcCHEtP(O)(OEt)}$ , on 128-9°,  $n_D^{20}$  1.4370,  $d_4^{20}$  1.0724. These alkylation products and  $\text{EtO}_2\text{CCH}_2\text{P(O)(OEt)}$  were added to esters and nitriles of unsat'd. carboxylic acids under the influence of  $\text{RONa}$  as catalyst; since these addns. were sluggish, a reflux period of 0.5-1 hrs. was necessary to attain the yields indicated below. Thus were obtained (b.p.,  $n_D^{20}$ , and  $d_4^{20}$

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given): 81.5% combined yield of  $(\text{EtO})_2\text{P}(\text{O})\text{CH}(\text{CO}_2\text{Et})\text{CH}_2\text{CH}_2\text{CO}_2\text{Me}$ ,  $b_p$  187-8°, 1.4410, 1.1368, and  $(\text{EtO})_2\text{P}(\text{O})\text{C}(\text{CO}_2\text{Et})(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})$ ,  $b_p$  199-200°, 1.4550, 1.1712; 22%  $(\text{EtO})_2\text{P}(\text{O})\text{CH}(\text{CO}_2\text{Et})\text{CH}_2\text{CH}_2\text{CN}$ ,  $b_p$  166-7°, 1.4418, 1.1045; 17%  $(\text{EtO})_2\text{P}(\text{O})\text{CH}(\text{CO}_2\text{Et})\text{CHMeCH}_2\text{CO}_2\text{Et}$ ,  $m$  75-8°; 67.8%  $(\text{EtO})_2\text{P}(\text{O})\text{CH}(\text{CO}_2\text{Et})\text{CHMeCH}_2\text{CN}$ ,  $b_p$  184°, 1.4458, 1.1144 (from vinylacetonitrile, which isomerized under action of the basic catalyst); 54% combined yield of  $(\text{EtO})_2\text{P}(\text{O})\text{CHAcCH}_2\text{CH}_2\text{CO}_2\text{Me}$ ,  $b_p$  186-2°, 1.4488, 1.1347, and  $(\text{EtO})_2\text{P}(\text{O})\text{C}(\text{Ac})(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})$ ,  $b_p$  188-92°, 1.4582, —; 47.5%  $(\text{EtO})_2\text{P}(\text{O})\text{CHAcCH}_2\text{CO}_2\text{Et}$ ,  $b_p$  183-4°, 1.4590, 1.1725; 10%  $(\text{EtO})_2\text{P}(\text{O})\text{CHAcC}(\text{CO}_2\text{Et})\text{CHCO}_2\text{Et}$ ,  $b_p$  183°, 1.4670, —; 70.5%  $(\text{EtO})_2\text{P}(\text{O})\text{CEtAcCH}_2\text{CH}_2\text{CN}$ ,  $b_p$  185°, 1.4577, 1.1022. Hydrolysis of several of the above esters resulted in formation of uncrystallizable sirups only. G. M. Kosolapoff.

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Anomalous reaction of  $\alpha$ -halo ketones with triethyl ester of phosphorous acid. A. N. Pydlovik (Chem. Inst., Acad. Sci. U.S.S.R., Kazan). *Dokl. Akad. Nauk SSSR* 25: 2173-82 (1955); cf. C.A. 50, 3219g. To 35 g. (EtO)<sub>3</sub>P (Ia) at 120° was added

dropwise 18.5 g. ClCH<sub>2</sub>Ac; after 1 hr. at 160° the mixt. was distd. yielding 23.8 g. (EtO)<sub>2</sub>P(O)CMe<sub>2</sub>CH<sub>2</sub> (I), b<sub>15</sub> 98°, n<sub>D</sub><sup>20</sup> 1.4190, d<sub>4</sub> 1.0709. I (10 g.) heated with 0.2 g. Na in 15 ml. dry EtOH gave a distillate of 1.55 g. Me<sub>2</sub>CO and 8.45 g. Ia. Hydrolysis of I with 30% H<sub>2</sub>SO<sub>4</sub> gave Me<sub>2</sub>CO and H<sub>3</sub>PO<sub>4</sub>. Ia (93 g.) mixed with 76.9 g. BrCH<sub>2</sub>Ac at 110-20° and heated 1 hr. at 150-70° gave 15 g. I and 75 g. AcCH<sub>2</sub>P(O)(OEt)<sub>2</sub> (II), b<sub>15</sub> 126°, n<sub>D</sub><sup>20</sup> 1.4350, d<sub>4</sub> 1.1252 (phenylhydrazone, b<sub>15</sub> 193°). Similarly 31 g. Ia and 25.6 g. BrCH<sub>2</sub>Ac in 50 ml. Et<sub>2</sub>O refluxed 3 hrs. gave 13.6 g. I and 4.6 g. II. Heating 40 g. Ia with 41 g. ICH<sub>2</sub>Ac in 100 ml. Et<sub>2</sub>O 1 hr. gave 33 g. II, 2.7 g. I, and 2.2 g. (EtO)<sub>2</sub>POH. BrCH<sub>2</sub>Bz (46.5 g.) and 40 g. Ia in 25 ml. C<sub>6</sub>H<sub>6</sub> reacted vigorously, then heated 0.5 hr. on a steam bath and distd. gave 34.7 g. BzCH<sub>2</sub>P(O)(OEt)<sub>2</sub> (III), b<sub>15</sub> 192-2.5°, n<sub>D</sub><sup>20</sup> 1.5137, d<sub>4</sub> 1.1790, and 0.1 g. (EtO)<sub>2</sub>P(O)CPhCH<sub>2</sub> (IV), b<sub>15</sub> 171°, n<sub>D</sub><sup>20</sup> 1.5009, d<sub>4</sub> 1.1422. Similarly 30 g. Ia and 32 g. BrCH<sub>2</sub>Bz in Et<sub>2</sub>O at reflux gave 21.6 g. III and 13.8 g. IV. Ia and ClCH<sub>2</sub>Bz at 130-40° gave only IV, while ICH<sub>2</sub>Bz in Et<sub>2</sub>O gave III and a little IV. IV and EtOH-EtONa slowly distd. gave AcPh, but III gave only a slight reaction with EtONa. Hydrolysis of III with 1:1 HCl at 140° gave BzCH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub>, m. 143°, which heated 6 hrs. at 220-30° with 1:1 HCl gave AcPh and H<sub>3</sub>PO<sub>4</sub>. IV

with 1:1 HCl rapidly yielded AcPh. 2-Chlorocyclohexanone (V) and Ia yielded on heating to 140° only *di-Et 1-cyclohexenyl phosphate*,  $b_p$  143°,  $n_D^{20}$  1.4523,  $d_4^{20}$  1.1032, which heated with EtOH-EtONa readily gave cyclohexanone and  $(EtO)_2PO$ . V (23 g.) and  $(EtO)_2PONa$ , from 3.8 g. Na, in Et<sub>2</sub>O gave 25.5 g. *di-Et cyclohexanone-2-phosphonate*,  $b_p$  126°,  $b_m$  146°,  $n_D^{20}$  1.4576,  $d_4^{20}$  1.1252; the free acid was a sirup; the phosphonate is much less rapidly hydrolyzed by HCl.

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*Chem* ✓ Synthesis of esters of phosphonic and thiophosphonic acids. XXIV. Addition of phosphonoacetonitrile and its homologs to esters and nitriles of unsaturated carboxylic acids. A. N. Pudovik and N. M. Lebedeva. *J. Gen. Chem. U.S.S.R.* 25, 2199-2202(1955)(Engl. translation).— See *C.A.* 50, 0280d. *R. M. R.* *Z*

PUDOVIK, A.N.

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Synthesis of esters of phosphonic and thionophosphonic acids. XXIV. Addition of phosphonoacetonitrile and its homologs to esters and nitriles of unsaturated carboxylic acids. A. N. Pudovik and N. M. Ichedeva. Zhur. Obshchei Khim. 29: 2235-40 (1955); cf. C.A. 49, 8788f; 50, 8442c. — To  $(EtO)_2P$  was added  $ClCH_2CN$  at 130–40°; distn. gave 80–5%  $(EtO)_2P(O)CH_2CN$  (I),  $b_1$  126–7°,  $n_D^{20}$  1.4310,  $d_4^{20}$  1.1312. This (7–10 g.) and equimolar amt. of unsatd. ester or nitrile treated with satd.  $EtONa-EtOH$  (1 drop to several ml.), then heated on a steam bath several hrs. gave the following esters (% yield, b.p.,  $n_D^{20}$ , and  $d_4^{20}$  given):  $(EtO)_2P(O)C(CN)CH_2CH_2CN$ , 82; — (m. 75–6°), —;  $(EtO)_2P(O)CH(CN)CHMeCH_2CN$ , 53.2,  $b_1$  170°, 1.4503, 1.1129;  $(EtO)_2P(O)CH(CN)CH_2CH_2CO_2Me$ ,  $b_1$  183–5°, 1.4470, 1.1570, and  $(EtO)_2P(O)C(CN)CH_2CH_2CO_2Me$ , 50.3 (combined),  $b_1$  195°, 1.4533, —;  $(EtO)_2P(O)CH(CN)CH_2CHMeCO_2Me$ ,  $b_1$  165–7°, 1.4410, 1.1175, and  $(EtO)_2P(O)C(CN)CH_2CHMeCO_2Me$ , 46.8 (combined),  $b_1$  177–80°, 1.4490, 1.1242;  $(EtO)_2P(O)CH(CN)CH_2CHMeCO_2Bu$ , 58,  $b_1$  100°, 1.4450, —;  $(EtO)_2P(O)CH(CN)CHMeCH_2CO_2Et$ , 40.5,  $b_1$  158–60°, 1.4440, 1.1058;  $(EtO)_2P(O)CH(CN)CH(CO_2Et)CH_2CO_2Et$ , 71.3,  $b_1$  194°, 1.4480, —;  $(EtO)_2P(O)CH(CN)CHPhCH_2CO_2Et$ , 26.3,  $b_1$  201–2°, 1.4815, 1.1250. I heated with K in  $Et_2O$ -dioxane

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1-2 hrs., followed by alkyl naltic and heating 3-6 hrs. gave the alkylated esters:  $(EtO)_2P(O)CHMeCN$ , 87.5,  $b_1$  140-1°, 1.4310, 1.0861;  $(EtO)_2P(O)CHPhCN$ , 53,  $b_1$  119°, 1.4328, 1.076;  $(EtO)_2P(O)CHPhCN$ , 73.5,  $b_1$  151°, 1.4385, 1.0578;  $(EtO)_2P(O)CHCNCHMe$ , 40.18,  $b_1$  140-7°, 1.4378, 1.0551;  $(EtO)_2P(O)CHBuCN$ , 49.4,  $b_1$  160-2°, 1.4378, 1.0401;  $(EtO)_2P(O)CH(CN)CH_2CH_2CH_3$ , 73.3,  $b_1$  154°, 1.4482, 1.0777;  $(EtO)_2P(O)CH(CN)CH_2CH_2Ph$ , 53,  $b_1$  170-1°, 1.5000, —;  $(EtO)_2P(O)C(CN)(CH_2Ph)_2$ , —,  $b_1$  210-15°, 1.5275, —. Addn. of these to unsatd. compounds with  $EtONa$  catalyst gave:  $(EtO)_2P(O)C(CN)CH_2CH_2CO_2Me$ , 90.8,  $b_1$  167°, 1.4490, 1.1120;  $(EtO)_2P(O)C(CN)(CH_2CHMeCO_2Bu)Pr$ , 75.2,  $b_1$  163°, 1.4480, 1.0381;  $(EtO)_2P(O)C(CN)(CH_2CH_2CN)CH_2CH_2CH_3$ , 42.6,  $b_1$  175°, 1.4620, 1.0977;  $(EtO)_2P(O)C(CN)Bu(CH_2CH_2CN)$ , 78.3,  $b_1$  180°, 1.4550, 1.0669.

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*PUDOVIK, A. N.*

USSR/Chemistry - Organic chemistry

Card 1/1 Pub. 22 - 27/51

Authors : Pudovik, A. N., and Lebedeva, N. M.

Title : About the reactions of chloro-and bromoacetone with triethylphosphite

Periodical : Dok. AN SSSR 101/5, 889-892, Apr 11, 1955

Abstract : The synthesis of phosphonium in two tautomeric forms as a product of reaction between chloro-and bromoacetone and triethylphosphite is announced. It was established that the methylene group in phosphonacetone is connected with the phosphonium and acetyl groups which should warrant sufficient mobility of its hydrogen atoms and also increase the ability of the phosphonacetone toward addition reactions. The physico-chemical properties of the triethylphosphite reaction products are listed. Eight references: 5 USSR, 2 USA and 1 German (1930-1954).

Institution : Acad. of Sc., USSR, Kazan Branch, The A. Ye. Arbuzov Chem. Inst.

Presented by : Academician B. A. Arbuzov, November 9, 1954

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Hypochlorination and oxidation of piperylene. Dokl. AN SSSR 103  
no.3:443-444 J1'55. (MIRA 8:11)

1. Kazanskiy gosudarstvennyy universitet imeni V.I.Ul'yanova-Lenina.  
Predstavleno akademikom B.A. Arbuzovym  
(Piperylene)

Pudovik, A. N.

Anomalous reaction of  $\alpha$ -halo ketones with esters of phosphorous acid, A. N. Pudovik (Kazan Branch, Acad. Sci., U.S.S.R.), Dokl. Akad. Nauk S.S.S.R. 185, 735-7 (1955); cf. C.A. 50, 3219c. At low temp. in  $\text{Et}_2\text{O}$ ,  $\text{ICH}_2\text{Ac}$  and  $(\text{EtO})_2\text{P}$  gave 82.0% of 90/10 mixt. of  $\text{AcCH}_2\text{PO}_2\text{Et}_2$  and  $\text{CH}_2\text{:CMcOPO}(\text{OEt})_2$ ;  $\text{BrCH}_2\text{Ac}$  similarly gave 20/80 mixt. while  $\text{ClCH}_2\text{Ac}$  at 100-20° (lower temp. does not induce the reaction) gave 93.9% isopropenyl ester.  $\text{BrCH}_2\text{Ac}$  or  $\text{ClCH}_2\text{Ac}$  at 155-60° gave 80% and 11.9% phosphate with a corresponding decline in yield of the unsatd. products were: ester. Other (RO)<sub>2</sub>P gave similar results. Prepd. were:  $\text{AcCH}_2\text{PO}(\text{OMe})_2$ , b<sub>p</sub> 123-4°, n<sub>D</sub><sup>20</sup> 1.4337, d<sub>4</sub> 1.1748;  $\text{CH}_2\text{:CMcOPO}(\text{OMe})_2$ , b<sub>p</sub> 84-5°, 1.4175, 1.1449;  $\text{AcCH}_2\text{PO}(\text{OBu})_2$ , b<sub>p</sub> 149-50°, 1.4315, 1.0152;  $\text{CH}_2\text{:CMcOPO}(\text{OBu})_2$ , b<sub>p</sub> 125-6°, 1.4268, 1.0049;  $(\text{iso-BuO})_2\text{P}(\text{O})\text{CH}_2\text{Ac}$ , b<sub>p</sub> 133-4°, 1.4335, 1.0246;  $(\text{iso-BuO})_2\text{POOCMe:CH:}$ , b<sub>p</sub> 122-3°, 1.4245, 0.9055. Reactions of  $\alpha$ , $\alpha$ - and  $\alpha$ , $\gamma$ -dihalo ketones yield mainly "anomalous" products;  $\text{AcCHCl}_2$  gave 70-83% diethyl 3-chloro-2-isopropenyl phosphate, b<sub>p</sub> 110.5-7°, 1.4370, 1.1833, and diethyl 3-chloro-2-isopropenyl phosphate, b<sub>p</sub> 154-5°, 1.4400, 1.0802. The former on chlorination gave 85% di-Et 1,2,3-trichloropropyl phosphate, b<sub>p</sub> 147-8°, 1.4550, 1.3414.  $\text{AcCHBr}_2$  gave similar results.  $\text{CO}(\text{CH}_2\text{Cl})_2$  and  $\text{CO}(\text{CH}_2\text{Br})_2$  gave  $\text{ClCH}_2\text{C}(\text{Cl})_2\text{OPO}(\text{OEt})_2$ , b<sub>p</sub> 133.5-4.5°, 1.4435, 1.1034, and the Br analog, b<sub>p</sub> 142.5-3°, 1.4622, 1.3028. Ozonolysis of these gave  $\text{CH}_2\text{O}$ , confirming the structure; chlorination confirmed the unsatn. Either of these 2 esters on further treatment with  $(\text{EtO})_2\text{P}$  gave  $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{Cl})_2\text{OPO}(\text{OEt})_2$ , b<sub>p</sub> 193-5°, 1.4435, 1.1623; transesterification of this with  $\text{EtOH}$

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*Pudovik, A. N.*

gave  $\text{Et}_2\text{PO}$  and  $\text{AcCH}_2\text{PO}(\text{OEt})_2$ . Halo ketones with more electroneg. substituents on the chain yield higher proportions of unsatd. phosphate product in reactions with  $(\text{RO})_2\text{P}$ .  $\text{Ac}_2\text{CHCl}$  gave 66-80%  $\text{MeC}(\text{CH}_2\text{Ac})\text{OPO}(\text{OEt})_2$ , b<sub>p</sub> 110-20°, 1.4489, 1.1237, and the *di-iso-Bu ester*, b<sub>p</sub> 137-8°, 1.4468, 1.0426. Dichloroacetylacetone gave 63% *di-Et chloroisopentenonyl phosphate*, b<sub>p</sub> 135°, 1.4626, 1.2292, or 80% *di-iso-Bu ester*, b<sub>p</sub> 150-1°, 1.4575, 1.1240; addn. of chlorine to the 1st of these gave 100% *di-Et tri-chloroisopentenonyl phosphate*, b<sub>p</sub> 151°, 1.4672, 1.3431.  $(\text{RO})_2\text{P}$  reacts readily with  $\text{AcCHClCH}_2\text{Et}$  or  $\text{AcCClCO}_2\text{Et}$ ; thus obtained were:  $\text{EtCO}_2\text{CH}(\text{CH}_2\text{CO}_2\text{OEt})_2$ , b<sub>p</sub> 155-6°, 1.4451, 1.1349; *di-iso-Bu ester*, b<sub>p</sub> 175°, 1.4445, 1.0569;  $\text{EtO}_2\text{CCCH}(\text{CH}_2\text{CO}_2\text{OEt})_2$ , b<sub>p</sub> 136°, 1.4572, 1.1203; *di-iso-Bu ester*, b<sub>p</sub> 154°, 1.4547, 1.1289. Treatment of  $\text{AcCH}_2\text{PO}(\text{OEt})_2$  with  $\text{SO}_2\text{Cl}_2$  gave 61%  $\alpha$ -chloro(diethylphosphono)acetone, b<sub>p</sub> 131-2°, 1.4484, 1.2233, which with  $(\text{EtO})_2\text{P}$  gave *di-Et diethylphosphonoisopentenyl phosphate*, b<sub>p</sub> 161-2°, 1.4478, 1.1762. The structures of the products were confirmed by chlorination, bromination and transesterification (cf. Perkow, et al., C.A. 50, 32134).

G. M. Kosolapoff

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Podovik, A. N.

Phosphonoethylation of mercaptans, dialkyl phosphonates and alkylphosphonic acids. A. N. Podovik and M. M. Zakharova (State Univ., Kazan). Doklady Akad. Nauk SSSR, 195, No. 3, 3-12 (1955). To 7 g.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{P(O)(OEt)}_2$  and 4.6 g.  $\text{PhSH}$  was gradually added satd.  $\text{EtONa}$  in  $\text{EtOH}$  maintaining the temp. below  $50-5^\circ$ ; distn. of the mixt. gave 7.8 g.  $\text{PhSCH}_2\text{CH}_2\text{P(O)(OEt)}_2$ ,  $b_p$   $203-4^\circ$ ,  $n_D^{20}$  1.5270,  $d_4^{20}$  1.1440 ( $n_D^{20}$  and  $d_4^{20}$  listed for the compds. below).  
Similarly, 1-methoxy-3-pentene-5-thiol gave 70%  $\text{MeOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{P(O)(OEt)}_2$ ,  $b_p$   $185-7^\circ$ , 1.4829, 1.0723; while 1-ethoxy-3-pentene-5-thiol gave 63%  $\text{EtOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{P(O)(OEt)}_2$ ,  $b_p$   $191-2^\circ$ , 1.4788, 1.0499, and 2-butene-4-thiol gave 65%  $\text{MeCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{P(O)(OEt)}_2$ ,  $b_p$   $120-2^\circ$ , 1.4680, 1.0136. Similar reaction of 5.8 g.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{P(O)(OEt)}_2$  and 5.5 g.  $(\text{EtO})_2\text{PSH}$  in the presence of  $\text{EtONa-EtOH}$  gave 7.8 g.  $(\text{EtO})_2\text{P(S)CH}_2\text{CH}_2\text{P(O)(OEt)}_2$ ,  $b_p$   $163^\circ$ , 1.4638, 1.1356;  $(\text{BuO})_2\text{PSH}$  gave 67%  $(\text{BuO})_2\text{P(S)CH}_2\text{CH}_2\text{P(O)(OEt)}_2$ ,  $b_p$   $209^\circ$ , 1.4510, 1.0573, while  $\text{EtP(O)H(OEt)}$  gave 59%  $\text{EtP(O)(OEt)CH}_2\text{CH}_2\text{P(O)(OEt)}_2$ ,  $b_p$   $195^\circ$ , 1.4510, 1.1235.  
G. M. Kosolapoff

PUDOVIK, A.N.

PUDOVIK, A.N.; ZAKHAROVA, M.M.

Phosphonoethylation of mercaptans of dialkylphosphorous acid and  
alkylphosphinous acid. Uch.zap.Kaz.un. 115 no.3:3-12 '55.  
(MLRA 10:5)

1.Kafedra sinteticheskogo kauchuka.  
(Mercaptans) (Phosphorous acid) (Phosphinous acid)

PUDOVIK, A.N. (Kazan')

Addition of incomplete esters of phosphorus acids to unsaturated  
compounds. Uch.zap.Kaz.un. 115 no.10:40-43 '55. (MLRA 10:5)  
(Phosphorus acids)  
(Unsaturated compounds)



PUDOVIK, A.N.; ARBUZOVA, M.P.

Synthesis and isomerization of phenyl ethers of ethoxy- and  
butoxypentenols. Uch.zap.Kaz.un. 116 no.1:136-140 '55.  
(MLRA 10:5)

1.Kafedra sinteticheskogo kauchuka.  
(Chemistry, Organic--Synthesis)  
(Isomerization) (Ether)

PUDOVIK, A.M.; IVANOV, B.Ye.

Addition of ethyl alcohol to isoprene oxide. Uch.zap.Kaz.un. 116  
no.1:141-144 '55. (MLRA 10:5)

1.Kafedra sinteticheskogo kauchuka.  
(Isoprene) (Rubber, Synthetic) (Ethyl alcohol)

PUDOVIK, A. N.  
USSR/General Questions

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Abs Jour: Ref Zhur-Khimiya No. 7, 1957, 21877

Author : Neslerova, N. M. and Pudovik A. N.

Inst : None

Title : Boris Aleksandrovich Arbuzov, (Bibliography)

Orig Pub: M. AN SSSR 1956, 48 p., 1 rouble

Abstract: No Abstract

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CHARTER, C. L.

"Anomalous Reaction of Haloketones with Esters of Thionic Acid"  
presented at the First Conference on Thionic Compounds,  
Tucson, 8-10 Dec 1961

8: P-3, 11.441

PUDOVIK, A. N.

✓ Anomalous reaction of  $\alpha$ -halo ketones with esters of phosphorous acid. II. Reaction of chloro- and bromoacetone with esters of phosphorous and phenylphosphonous acids. A. N. Pudovik and V. P. Aver'yanova (State Univ., Kazan). *Zhur. Obshchei Khim.* 26, 1426-31 (1950); cf. C.A. 50, 8486i. — Dropwise addn. of 22.1 g.  $\text{AcCH}_2\text{Br}$  to 20 g.  $(\text{MeO})_2\text{P}$  preheated to 110–15°, followed by 0.5 hr. at 120° gave 10.5 g.  $(\text{MeO})_2\text{P}(\text{O})\text{OCMe:CH}_3$  (I), b<sub>p</sub> 84–5°, d<sub>20</sub> 1.1449, n<sub>D</sub><sup>20</sup> 1.4175, and 8.4 g.  $(\text{MeO})_2\text{P}(\text{O})\text{CH}_2\text{Ac}$  (II), b<sub>p</sub> 123–4°, d<sub>20</sub> 1.1748, n<sub>D</sub><sup>20</sup> 1.4337. Careful heating of 24 g.  $(\text{MeO})_2\text{P}$  and 25.2 g.  $\text{AcCH}_2\text{Cl}$  to 70° started a vigorous reaction kept at 80° by cooling; distn. gave 30 g. I and 1.7 g. II; a similar reaction at 110° gave, from 30 g.  $(\text{MeO})_2\text{P}$ , 25.4 g. I and 0.6 g. II. Distn. of 0.2 g. Na in 15 ml. dry MeOH and 10 g. I gave MeOH and  $\text{Me}_2\text{CO}$ , as well as 2.5 g.  $(\text{MeO})_2\text{PO}$ . Heating 40 g.  $(\text{EtO})_2\text{P}$  and 22 g.  $\text{AcCH}_2\text{Cl}$  to 95° started a vigorous reaction completed by 0.5 hr. at 110–20°, yielding 26 g. *di-Et* analog of I and 1.7 g. *di-Et* analog of II, b<sub>p</sub> 127–9°, n<sub>D</sub><sup>20</sup> 1.4350; slow addn. of 13.8 g.  $\text{AcCH}_2\text{Cl}$  to 25 g. refluxing  $(\text{EtO})_2\text{P}$  gave 2.7 g. *di-Et* analog of II and 20 g. *di-Et* analog of I. Ozonization of the *di-Et* analog of I in  $\text{CCl}_4$  and treatment with hot  $\text{H}_2\text{O}$  gave  $\text{CH}_3\text{O}$ . Heating 30 g.  $(\text{BuO})_2\text{P}$  and 11 g.  $\text{AcCH}_2\text{Cl}$  to 135–45° gave 15.8 g.  $(\text{BuO})_2\text{P}(\text{O})\text{OCMe:CH}_3$ , b<sub>p</sub> 125–6°, d<sub>20</sub> 1.0049, n<sub>D</sub><sup>20</sup> 1.4268, and 2.5 g.  $(\text{BuO})_2\text{P}(\text{O})\text{CH}_2\text{Ac}$ , b<sub>p</sub> 149–50°, n<sub>D</sub><sup>20</sup> 1.4322. Addn. of 10.4 g.  $\text{AcCH}_2\text{Br}$  to 30 g.  $(\text{BuO})_2\text{P}$  at 145–55° gave 7.6 g.  $(\text{BuO})_2\text{P}(\text{O})\text{OCMe:CH}_3$ , and 13.9 g.  $(\text{BuO})_2\text{P}(\text{O})\text{CH}_2\text{Ac}$ , b<sub>p</sub> 137–8°, d<sub>20</sub> 1.0152, n<sub>D</sub><sup>20</sup> 1.4315. Heating 40 g.  $(\text{iso-BuO})_2\text{P}$  with 15 g.  $\text{AcCH}_2\text{Cl}$  to 115–20°, finally 125°, gave 30 g.  $(\text{iso-BuO})_2\text{P}(\text{O})\text{OCMe:CH}_3$ , b<sub>p</sub> 122–3°, d<sub>20</sub> 0.9955, n<sub>D</sub><sup>20</sup> 1.4245, and 2 g.  $(\text{iso-BuO})_2\text{P}(\text{O})\text{CH}_2\text{Ac}$ , b<sub>p</sub> 145–7°, n<sub>D</sub><sup>20</sup> 1.4330; the same reaction at 160° gave 25.7 g. phosphate ester and 0 g. phosphonate; slow addn. of 10.9 g.  $\text{AcCH}_2\text{Br}$  to 20 g.  $(\text{iso-BuO})_2\text{P}$  at 155° gave 2.5 g. phosphate ester and 9.5 g. phosphonate, b<sub>p</sub> 133–4°, d<sub>20</sub> 1.0246, n<sub>D</sub><sup>20</sup> 1.4335; the former distd. with  $\text{iso-BuONa}$ - $\text{iso-BuOH}$  gave

Pudovik, A. N., AVER'YANOVA, V. P.

Me<sub>2</sub>CO and (iso-BuO)<sub>2</sub>PO, b<sub>12</sub> 134-5°, n<sub>D</sub><sup>20</sup> 1.4195, d<sub>4</sub> 0.985. Hydrolysis of diisobutylpropenyl phosphate with 30% H<sub>2</sub>SO<sub>4</sub> readily gave Me<sub>2</sub>CO. To 28 g. PhP(OMe)<sub>2</sub>, preheated to 90° was slowly added 15.2 g. AcCH<sub>2</sub>Cl (vigorous action) and after completion of reaction under 120° there was obtained 18.5 g. PhP(O)(OMe)OCH<sub>2</sub>CH<sub>3</sub> (III), b<sub>12</sub> 137-8°, d<sub>4</sub> 1.1421, n<sub>D</sub><sup>20</sup> 1.5120, and 2.5 g. material b<sub>12</sub> 165-70°, n<sub>D</sub><sup>20</sup> 1.5216; under these conditions AcCH<sub>2</sub>Br gave only tar. Reaction of 20 g. PhP(OMe)<sub>2</sub> and 18 g. AcCH<sub>2</sub>Br in Et<sub>2</sub>O gave 3.8 g. III, b<sub>12</sub> 137-9°, n<sub>D</sub><sup>20</sup> 1.5135, and 5 g. PhP(O)(CH<sub>2</sub>Ac)OMe, b<sub>12</sub> 189-70°, d<sub>4</sub> 1.1965, n<sub>D</sub><sup>20</sup> 1.5220, with much tar. To (EtO)<sub>2</sub>PONa from 100 g. (EtO)<sub>2</sub>POH, 14.4 g. Na, and 200 ml. Et<sub>2</sub>O was slowly added 57.6 g. AcCH<sub>2</sub>Cl; after 3 hrs. refluxing and centrifugal sepn. of NaCl there was obtained 50 g. product, b<sub>12</sub> 50-94°, 6 g. product, b<sub>12</sub> 94-8°, and 7 g. product, b<sub>12</sub> 122-9°, n<sub>D</sub><sup>20</sup> 1.4345; it was impossible to isolate individual products. Similar reaction with 50 g. (EtO)<sub>2</sub>POH, 7 g. Na, and 42.8 g. AcCH<sub>2</sub>Br in ligroine gave 9 g. (EtO)<sub>2</sub>P(O)CH<sub>2</sub>Ac, b<sub>12</sub> 131°, n<sub>D</sub><sup>20</sup> 1.4320, and lower boiling fractions; the results were the same in Et<sub>2</sub>O, C<sub>6</sub>H<sub>6</sub>, or MePh.

G. M. Kosolapoff

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Pudovik, A.N.

III. Reaction of  $\alpha,\alpha$ - and  $\alpha,\gamma$ -dibromo ketones with triethyl phosphite. A. N. Pudovik and L. G. Silekhova (State Univ., Kazan). *Dokl. Akad. Nauk SSSR*, 26, 1431-2 (1939). — Addn. of 40 g.  $(EtO)_3P$  to 31.3 g.  $CO(CH_2Cl)_2$  preheated to  $120^\circ$  gave 25.2 g.  $(EtO)_2P(O)OC(CH_2Cl)_2$ ;  $b_p$  133.5–1.5°,  $d_4^{20}$  1.1934,  $n_D^{20}$  1.4435, and 4.5 g. higher-boiling fraction which was not purified. Chlorination of above unsatd. ester in  $CCl_4$  with ice cooling gave a good yield of  $(EtO)_2P(O)OCCl(CH_2Cl)_2$ ;  $b_p$  150–2°,  $d_4^{20}$  1.3593,  $n_D^{20}$  1.4631. Addn. of 63 g.  $(EtO)_3P$  to 80.0 g.  $CO(CH_2Br)_2$  preheated to  $120^\circ$  gave 40 g.  $EtBr$  and 42.2 g.  $(EtO)_2P(O)OC(CH_2Br)_2$ ;  $b_p$  142.5–3°,  $d_4^{20}$  1.3028,  $n_D^{20}$  1.4622; the residue was undistillable. A similar reaction at  $20-6^\circ$  gave only the unsatd. ester above. Chlorination of the unsatd. ester as above gave a good yield of  $(EtO)_2P(O)OCCl(CH_2Br)_2$ ;  $b_p$  159°,  $d_4^{20}$  1.5103,  $n_D^{20}$  1.4733. Ozonolysis of II gave  $CH_2O$ . Heating 7.45 g. I with 7 g.  $(EtO)_3P$  4 hrs. at  $240^\circ$  in sealed tube gave 5.4 g.  $(EtO)_2P(O)OC(CH_2)_2$ ;  $b_p$  193–5°,  $d_4^{20}$  1.1623,  $n_D^{20}$  1.4435, which formed readily from II and  $(EtO)_3P$  refluxed 5 hrs.; the product in this case,  $b_p$  195–7°,  $d_4^{20}$  1.1645,  $n_D^{20}$  1.4440. Mixing 25.2 g.  $AcCHCl_2$  and 33.2 g.  $(EtO)_3P$  gave a spontaneous reaction (temp. rise to  $120^\circ$ ); final heating to  $110^\circ$  completed the reaction yielding 37.3 g.  $(EtO)_2P(O)OCMe_2CHCl_2$ ;  $b_p$  116.5–17°,  $d_4^{20}$  1.1833,  $n_D^{20}$  1.4370, which chlorinated in  $CCl_4$  with ice cooling to a good yield of  $(EtO)_2P(O)OCClMe_2CHCl_2$ ;  $b_p$  147–8°,  $d_4^{20}$  1.3414,  $n_D^{20}$  1.4580. A similar reaction of 15 g.  $(BuO)_3P$  with 8 g.  $AcCHCl_2$  gave 13.6 g.

*A.M. PUDOVIN AND L.G. SALEKHOVA*

(BuO)<sub>3</sub>P(O)OCMe: CHCl<sub>3</sub>, b<sub>m</sub> 164-5°, d<sub>20</sub> 1.0892, n<sub>D</sub><sup>20</sup> 1.4400.  
Heating 0.2 g. Na in 15 ml. dry EtOH with 5.4 g. (EtO)<sub>3</sub>P-  
(O)OC(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>P(O)(OEt)<sub>2</sub> gave 0.7 g. (EtO)<sub>3</sub>PO and 0.8  
g. (EtO)<sub>3</sub>P(O)CH<sub>2</sub>Ac, b<sub>m</sub> 130-7°, n<sub>D</sub><sup>20</sup> 1.4352. Addn. of 30  
g. CO(CH<sub>2</sub>Br)<sub>2</sub> to an Et<sub>2</sub>O soln. of 6.3 g. Na in 38.3 g.  
(EtO)<sub>3</sub>POH gave after sepn. of NaBr 9.5 g. unidentified  
halogen-free product, b<sub>m</sub> 87-9°, d<sub>20</sub> 1.0024, n<sub>D</sub><sup>20</sup> 1.4000, and a  
1.1-g. fraction, b<sub>m</sub> 117-27°, d<sub>20</sub> 1.0914, n<sub>D</sub><sup>20</sup> 1.4310. To 26  
g. AcCHBr<sub>2</sub> at 120° was added 20 g. (EtO)<sub>3</sub>P with cooling;  
there was formed 11.8 g. (EtO)<sub>3</sub>P(O)OCMe: CHBr, b<sub>m</sub> 120-  
7°, d<sub>20</sub> 1.3043, n<sub>D</sub><sup>20</sup> 1.4610, which chlorinated as above gave a  
good yield of (EtO)<sub>3</sub>P(O)OCMeClCHBrCl, b<sub>m</sub> 164-5°, d<sub>20</sub>  
1.4007, n<sub>D</sub><sup>20</sup> 1.4735.

G. M. Kosolapoff

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PUDOVIK, A. N.

Anomalous reaction of  $\alpha$ -halo ketones with esters of phosphorous acid. II. Reaction of chloro- and bromoacetone with esters of phosphorous and phenylphosphonous acids. A. N. Pudovik and V. P. Aver'yanova. *J. Gen. Chem. U.S.S.R.* 26, 1808-9 (1950) (English translation). — See C.A. 50, 14512f. III. Reaction of  $\alpha,\alpha$ - and  $\alpha,\gamma$ -dihalo ketones with triethyl phosphite. A. N. Pudovik and L. G. Salekhova. *Ibid.* 1811-14. — See C.A. 50, 14513c. B.M.R.

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*Handwritten: Pudovik, A.N.*  
PUDOVIK, A.N.; ALTUNINA, N.

Addition of  $\alpha$ -haloethers to isoprene. Zhur.ob.khim. 26 no.6:  
1635-1639 Je '56. (MIRA 11:1)

1.Kazanskiy gosudarstvennyy universitet,  
(Isoprene) (Ethers)

PUDOVIK, A.N.

Chem ✓ New method of synthesis of esters of phosphonic and thiophosphonic acids. XXV. Addition of mixed dialkyl phosphites, dialkyl thiophosphites and dialkyl phosphite to unsaturated compounds. A. N. Pudovik and N. I. Khlyupina (State Univ., Kazan). *Zhur. Obshch. Khim.* 26, 1072-7 (1950); cf. *C.A.* 50, 9380d. — Heating 1 mole  $(EtO)_2PSH$  with 1.5-2.5 moles ROH with a few drops of  $H_2PO_4$  2 hrs. at 150-65° gave the following esters: 32%  $EtO(BuO)PSH$ , b. 72-3°,  $n_D^{20}$  1.4040,  $d_4^{20}$  1.0325; 31.5%  $EtO(iso-BuO)PSH$ , b. 70-2°, 1.4605, 1.0287; 38.7%  $EtO(iso-AmO)PSH$ , b. 81.5-2.5°, 1.4480, 1.0032. An equimolar mixt. of one of the above esters and the desired unsatd. compd. was slowly treated with satd.  $EtONa-EtOH$  until the exothermic reaction ceased, heated 0.5 hr. on a steam bath, and the products were distd. Thus esters of methacrylic, cinnamic and maleic acids,  $CH_2=CHMeCN$ , mesityl oxide, and various anils yielded the following products: (Y, % yield, b.p./mm. or m.p.,  $n_D^{20}$  and  $d_4^{20}$  given):  $EtO(BuO)P(O)Y$ :  $CH_2=CHMeCO_2Bu$ , 69.3, 155-8°/10, 1.4335, 1.0124;  $CH_2=CHMeCO_2Et$ , 54.1, 177-8°/8, 1.4807, 1.0974;  $CH_2=CHMeCO_2Me$ , 55, 178-8.5° (sic), 1.4405, 1.1435;  $CH_2=CHMeCN$ , 59.7, 170°/10, 1.4450, 1.0577;  $CH_2=CHAc$ , 80.6, 135-6°/10, 1.4390, 1.0145;  $CH(C_6H_4NO_2-m)NHCH_2Me-m$ , 49.1, m. 122°.

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PUDOVIK, A. N.

Pudovik A. N., Khlyupina N. I.

$\text{CH}(\text{NHPh})\text{CH}_2\text{NMe}_2$ , p. 45.6, m. 98°.  $\text{CH}_2\text{CHMeCO}_2\text{Bu}$ , 70.6, 148°/10, 1.4635, 1.0362;  $\text{CH}_2\text{CHMeCN}$ , 57.3, 176°/10, 1.4350, 0.9767.  $\text{EtO}(\text{iso-AmO})\text{P}(\text{O})\text{CMe}_2\text{CH}_2\text{Ac}$ , 79.2%, b. 153-4°/10,  $n_D^{20}$  1.4010,  $d_4^{20}$  0.9977. Similarly  $(\text{CH}_2)_2\text{CHCH}_2\text{O}_2\text{P}(\text{O})\text{H}$  gave the following:  $(\text{CH}_2)_2\text{CHCH}_2\text{O}_2\text{P}(\text{O})\text{Et}$ , % yield, b.p./mm. or m.p.,  $n_D^{20}$ ,  $d_4^{20}$  given:  $\text{CH}_2\text{CHMeCO}_2\text{Me}$ , 67.3, 143-4°/8, 1.4306, 1.0753;  $\text{CH}_2\text{CHMeCO}_2\text{Bu}$ , 65, 170-7°/8, 1.4582, 1.0573;  $\text{CH}(\text{CO}_2\text{Me})\text{CH}_2\text{CO}_2\text{Me}$ , 67.3, 185°/8, 1.4300, 1.1120;  $\text{CHPhCH}_2\text{CO}_2\text{Et}$ , 62.3, 201-1.5°/8, 1.4960, 1.1180;  $\text{CH}(\text{C}_6\text{H}_5\text{NO}_2\text{-m})\text{NHCH}_2\text{Me}$ , 53.7, —;  $\text{CHNH}(\text{NHPh})\text{C}_6\text{H}_5\text{NMe}_2$ , p. 59.5, — (no phys. consts. for the last 2 compds. given). Treatment of crotyl alc. or  $\text{CH}_2\text{CHCH}(\text{OH})\text{Me}$  with  $\text{PCl}_5$  failed to yield any  $(\text{RO})_2\text{POH}$ , as only

$\text{RCl}$  and  $\text{H}_3\text{PO}_4$  were obtained. In the prepn. of  $(\text{CH}_2)_2\text{CHCH}_2\text{O}_2\text{P}(\text{O})\text{H}$  the use of dry allyl alc. and termination of the distn. of the product after some 2/3 of the material had been distd. are said to be effective means for the prevention of explosions in distn. of the ester. G. M. Kosolapoff.

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PUDOVIK, AN.

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Addition of  $\alpha$ -halo ethers to isoprene. A. N. Pudovik  
and N. Altunbas. J. Gen. Chem. U.S.S.R. 26, 1833-4  
(1956) (English translation).—See C.A. 51, 1834h.

B. M. R.

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PUDOVIK, A.N.

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New method of synthesis of esters of phosphonic and  
thiophosphonic acids. 722V. Addition of mixed dialkyl  
phosphites, dialkyl thiophosphites, and dialkyl phosphite to  
unsaturated compounds. A. N. Pudovik and N. I. Kiselev  
pina. J. Gen. Chem. U.S.S.R. 20, 1877-80 (1955) (English  
translation).—See *Chem. Abstr.* 51, 8439f. B. M. R.

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Pudovik, A. N.

Hypochlorination of piperylene. A. N. Pudovik and B. E. Ivanov (State Univ., Kazan). *Zhur. Obshchei Khim.* 26, 1910-14 (1956); cf. *C.A.* 50, 5522f. — HOCl adds to

piperylene in 1,2-, 3,4-, and 1,4-positions. Through a suspension of 400 g. chlorinated lime in 5 l. H<sub>2</sub>O was passed at 0° for 0.5 hr. a strong stream of CO<sub>2</sub> and 400 g. piperylene; was added over 3 hrs.; the mixt. was filtered, satd. with NaCl and extd. with Et<sub>2</sub>O yielding 230 g. products, which on fractionation gave 25 g. 3-chloro-4-penten-3-ol (I), b<sub>p</sub> 60-1°, n<sub>D</sub><sup>20</sup> 1.4570, d<sub>4</sub> 1.0584, 7 g. 5-chloro-2-penten-4-ol (II), b<sub>p</sub> 66-7°, n<sub>D</sub><sup>20</sup> 1.4685, d<sub>4</sub> 1.0720, and 21 g. 5-chloro-3-penten-2-ol (III), b<sub>p</sub> 82-2.5°, n<sub>D</sub><sup>20</sup> 1.4700, d<sub>4</sub> 1.0835. Their structures were confirmed by oxidation and ozonolysis. I and Br in CHCl<sub>3</sub> gave 1,2-dibromo-3-chloro-4-pentanol, b<sub>p</sub> 136-8°, n<sub>D</sub><sup>20</sup> 1.5470; III and Br gave 1-chloro-2,3-dibromo-4-pentanol, b<sub>p</sub> 140-9°, m. 69-70°. I heated with Ac<sub>2</sub>O in C<sub>6</sub>H<sub>6</sub> gave the corresponding acetate, b<sub>p</sub> 66-7°, n<sub>D</sub><sup>20</sup> 1.4365, d<sub>4</sub> 1.0604; III gave the acetate, b<sub>p</sub> 80-9.5°, n<sub>D</sub><sup>20</sup> 1.4555, d<sub>4</sub> 1.0790. I and 60% KOH at 160° gave 50% 2,3-epoxy-4-pentene, b. 82-3°, n<sub>D</sub><sup>20</sup> 1.4135, d<sub>4</sub> 0.8464. II gave 1,2-epoxy-3-pentene, b. 103-4°, n<sub>D</sub><sup>20</sup> 1.4345, d<sub>4</sub> 0.8750, while III gave only tarry products. At 50° in 0.1M aq. soln. in 8 hrs. 41% I hydrolyzes, 47% III, and 7% II.

G. M. K.

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PUDOVIK, A.N.

Anomalous reaction of  $\alpha$ -haloketones with phosphorous esters. Part 4:  
Reaction of phosphorous esters with mono- and dichloroacetylacetone,  
phosphonoacetone and acetoacetic ester. Zhur. ob. khim. 26 no.8:2238-  
2243 Ag '56. (MLRA 10:11)

1. Kazanskiy gosudarstvennyy universitet.  
(Ketones) (Phosphorous acids)



*Pudovik, A. N.*

*1*  
✓ Anomalous reaction of  $\alpha$ -keto ketones with esters of phosphorous acid. *IV*. Reactions of esters of phosphorous acid with mono- and dichloroacetylacetone, phosphonoacetone, and acetoacetic ester. A. N. Pudovik. *J. Gen. Chem. U.S.S.R.* 26, 2503-8 (1958) (English translation). See *C.A.* 51, 1827b.

*B. M. R.*

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PUDOVIK, A.N.; IVANOV, B.Ye.

Addition reactions with  $\alpha$ -oxides of pentadiene. Zhur. ob. khim.  
26 no.10:2768-2771 0 '56. (MIRA 11:3)

1. Kazanskiy Gosudarstvennyy universitet.  
(Pentadienes) (Hydrolysis)

Pudovik, A. N.

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Oxidation of butadiene, isoprene and piperylene with acetyl hydroperoxide. A. N. Pudovik and B. E. Ivanov (State Univ., Kazan). *Zhur. Obshch. Khim.* 28, 2771-3 (1956). The rate of oxidation of dienes with  $\text{AcO}_2\text{H}$  rises in the series: butadiene, isoprene, *cis*- and *trans*-piperylene, 2,3-dimethylbutadiene, 2,4-hexadiene. The accumulation of Me groups at the terminal C atoms of butadiene accelerates the reaction more than does a similar accumulation in the middle of the mol. The reaction rate curves are shown. Treatment of 60 g. butadiene in 2 l.  $\text{Et}_2\text{O}$  with 80 ml. 90%  $\text{AcO}_2\text{H}$  at room temp. in 15 days gave 35 g. 1,2-epoxy-3-butene; b. 68-6.5°, d<sub>4</sub> 0.8720, n<sub>D</sub><sup>20</sup> 1.4105. Similarly, isoprene with 95%  $\text{AcO}_2\text{H}$  in 12 days gave 1,2-epoxy-2-methyl-1-butene, b. 70.5-80.5°, d<sub>4</sub> 0.8574, n<sub>D</sub><sup>20</sup> 1.4180. Mixed *cis-trans*-piperylenes (170 g.) in 6 l.  $\text{Et}_2\text{O}$  with 200 ml. 80%  $\text{AcO}_2\text{H}$  in 9 days gave mixed products: 45 g. mixed *cis-trans*-3,4-epoxypentene, b. 82-6°, d<sub>4</sub> 0.8472, n<sub>D</sub><sup>20</sup> 1.4140, and 34 g. mixed *cis-trans*-1,2-epoxy-3-pentene, b. 102-6°, d<sub>4</sub> 0.8752, n<sub>D</sub><sup>20</sup> 1.4355. Pure *cis*-piperylene gave the *cis*-3,4-epoxypentene, b. 84.5-6°, d<sub>4</sub> 0.8592, n<sub>D</sub><sup>20</sup> 1.4182, and *cis*-1,2-epoxy-3-pentene, b. 103-4°, d<sub>4</sub> 0.8953, n<sub>D</sub><sup>20</sup> 1.4385, while *trans*-piperylene gave *trans*-3,4-epoxypentene, b. 82-3.5°, d<sub>4</sub> 0.8432, n<sub>D</sub><sup>20</sup> 1.4110, and *trans*-1,2-epoxy-3-pentene, b. 101-2°, d<sub>4</sub> 0.8720, n<sub>D</sub><sup>20</sup> 1.4325. Piperylene (68 g.) in 4 l.  $\text{Et}_2\text{O}$  and 100 ml. 85%  $\text{AcO}_2\text{H}$  in 17 days gave 12 g. 3,4-epoxy-1-pentene, 7 g. 1,2-epoxy-3-pentene, and 7 g. piperylene dioxide, b. 66-7°, d<sub>4</sub> 1.0278, n<sub>D</sub><sup>20</sup> 1.4295. G. M. K.

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PUDOVIK, A. N.

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New method of synthesis of esters of phosphonic and thiophosphonic acids. XXVI. Addition of partial esters of acids of phosphorus to ethyl isocyanate, vinyl acetate, and esters of unsaturated carboxylic acids. A. N. Pudovik, I. V. Koudonova, and R. S. Kravchenko (State Univ., Kazan). *Zhur. Obshchei Khim.* 26, 3110-16 (1956); cf. *C.A.* 49, 9476i; 50, 4808b; 51, 3439f. Mixing of  $(RO)_2POH$ ,  $RPH(O)OR$ , or  $(RO)_2PSH$  with  $EtNCO$  resulted in a slight elevation of temp. but the reaction is evidently very slow. Addn. of dry  $RONa$  produced an exothermic reaction, yielding the following esters: 68%  $EtNHCOPO(OEt)_2$ ,  $b_p$  107-8°,  $n_D^{20}$  1.4465,  $d_4^{20}$  1.1294; 65%  $EtNHCOPO(OEt)OBu$ ,  $b_p$  177°,  $n_D^{20}$  1.4581,  $d_4^{20}$  1.0589; 39%  $EtNHCOPO(S)(OEt)_2$ ,  $b_p$  166-8°,  $n_D^{20}$  1.4811,  $d_4^{20}$  1.1393. Addn. of  $(RO)_2POH$  to esters of HCNS and phenyl and allyl mustard oils in the presence of  $EtONa$  resulted in an apparent reaction in each case but the products decomposed during attempted distn. Addn. of  $RONa$  to equimolar mixts. of  $AcOCH_2CH_2$  and either  $(RO)_2PSH$  or  $RPH(O)OR$  gave similarly: 48%  $EtOPE(O)CH_2CH_2OAc$ ,  $b_p$  110-11°,  $n_D^{20}$  1.4301,  $d_4^{20}$  1.0704; 51.5%  $BuOPE(O)CH_2CH_2OAc$ ,  $b_p$  123°,  $n_D^{20}$  1.4412,  $d_4^{20}$  1.0408; 35%  $EtOPP(O)CH_2CH_2OAc$ ,  $b_p$  149-50°,  $n_D^{20}$  1.4990,  $d_4^{20}$  1.1329; 33%  $(EtO)_2P(S)CH_2CH_2OAc$ ,  $b_p$  125-7°,  $n_D^{20}$  1.4500,  $d_4^{20}$  1.1107 (the mixt. in this case must be heated preliminarily with  $Et_3N$  for a satisfactory reaction (cf. above refs.)). Reaction of  $AcOCH_2CH_2$  with  $(EtO)_2P(O)CH_2CO_2Et$ ,  $(EtO)_2P(O)CH_2Ac$ , and  $(EtO)_2P(O)CH_2CN$  was performed similarly in the presence of  $EtONa$ , requiring 2 hrs. on a steam bath for completion; however, attempted distn. gave either starting materials or decompn. products and tar. Addn. of partial esters of appropriate acids of P to unsatd. carboxylic esters

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A.N. PUDOVIK, I.V. KONVALOVA, R.E. KRIVONOSOVA

gave the following: 84.5%  $(EtO)_2P(O)CH_2(CO_2Et)CH_2CO_2Et$ ,  $b_p$  182°,  $n_D^{20}$  1.4385,  $d_4^{20}$  1.1105; 40%  $(EtO)_2P(S)CH_2(CO_2Et)CH_2CO_2Et$ ,  $b_p$  180-1°,  $n_D^{20}$  1.4508,  $d_4^{20}$  1.1206; 20.1%  $(iso-BuO)_2P(S)CH_2(CO_2Et)CH_2CO_2Et$ ,  $b_p$  166-7°,  $n_D^{20}$  1.4620,  $d_4^{20}$  1.0840; 43.8%  $(EtO)_2P(O)CHMeCHMeCO_2Et$ ,  $b_p$  142-3°,  $n_D^{20}$  1.4330,  $d_4^{20}$  1.0616; 21%  $(MeO)_2P(O)CHMeCH_2CO_2Et$ ,  $b_p$  121-3°,  $n_D^{20}$  1.4260,  $d_4^{20}$  1.0821; 18.6%  $(EtO)_2P(O)CHMeCH_2CO_2Et$ ,  $b_p$  121-2°,  $n_D^{20}$  1.4310,  $d_4^{20}$  1.0623. Addn. of  $(RO)_2P(O)H$  to  $PhMeC:CHCO_2Et$ ,

and of  $(EtO)_2P(O)CH_2CO_2Et$  to di-Bt citraconate failed.  
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USSR/Organic Chemistry - Synthetic Organic Chemistry

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Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 4297

Author : Pudovik, A.N., Arbuzova, M.P.

Inst : Kazan University

Title : Synthesis and Isomerization of Phenol Ethers of  
Ethoxy- and Butoxyphenols

Orig Pub : Uch. zap. Kazanskogo un-ta, 1956, 116, No 1, 136-140

Abstract : Study of interaction of  $RCCH_2CH_2CH=CHCH_2Cl$  (I)  $R = C_2H_5$   
or  $C_4H_9$ , and  $C_2H_5OCH_2CH_2CHClCH=CH_2$  (II) with  $C_6H_5OH$   
(III) and  $KCH$ . In aqueous media I and II form  
 $ROCH_2CH_2CH=CHCH_2OC_6H_5$  (IV). In acetone solution II yields,  
in addition to IV ( $R = C_2H_5$ ), also  $C_2H_5-OCH_2CH(OC_6H_5)CH=$   
 $CH_2$  (V).

Card 1/3

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FUDOVİK, A. N. (Chem. Inst. im. Acad. A. Ye. Arbuzov, Kazan Affil. AS USSR)

"The Anomalous Reaction of alpha-halogen ketones with Complete Esters of Phosphorous Acid" (Ob anomal'noy reaktsii alpha-galoidketonov s polnymi efirami fosforistoy kisloty)

Chemistry and Uses of Organophosphorous Compounds  
(Khimiya i primeneniye fosfororganicheskikh soedneniy),  
Trudy of First Conference, 8-10 December 1955, Kazan,  
PP. Published by Kazan Affil. AS USSR, 1957  
248-261

Report discussed by M. I. Kabachnik (Inst. Element. Organ. Compounds AS USSR),  
B. A. Arbuzov (Chem. Inst. im. Acad. A. Ye. Arbuzov, Kazan Affil. AS USSR), and  
by author.

*Pudovik, A.N.*

USSR/General Topics - Methodology, History, Scientific  
Institutions and Conferences, Instruction, Problems  
Concerning Bibliography and Scientific Documentation.

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Abs Jour : Referat Zhur - Khimiya, No 1, 1958, 12.

Author : A.N. Pudovik

Inst : -

Title : A Glorious Anniversary.

Orig Pub : Zh. obshch. khimii, 1957, No 9, 2313-2328

Abstract : To the 80th anniversary of the birthday and the 50th  
anniversary of the scientific activity of academician  
A.Ye. Arbuzov.

Biographical sketch and scientific works.

Bibliography with 64 titles.

Card 1/1



Pudovik, A. N.

V New method of synthesis of esters of phosphonic and thiophosphonic acids. XVIII. Addition of dialkyl phosphites and dialkyl thiophosphites to the yellow derivatives of malonic ester and acetylacetic. Phosphonoacetic acids. A. N. Pudovik and T. M. Moshkina (State Univ., Kazan). Zh. Obshch. Khim. 27, 1611-17 (1957); Ch. 47, 99105; 48, 2573c; 50, 41437, 11230f; 51, 8542c; Goldstein and Fiebig, C.A. 51, 5769c. To an equimolar mixt. of  $\text{CH}_2\text{C}(\text{CO}_2\text{Et})_2$  (cf. Levina and Golovnikov, C.A. 50 2458c) and  $(\text{RO})_2\text{POH}$  or  $(\text{RO})_2\text{PSH}$  was added a satd. soln. of  $\text{RONa}$  in  $\text{ROH}$ ; after the exothermic reaction the mixt. was warmed 15-20 min. on an  $\text{H}_2\text{O}$  bath and distd. yielding: 88%  $(\text{MeO})_2\text{P}(\text{O})\text{CH}_2\text{CH}(\text{CO}_2\text{Et})_2$ ,  $b_p$  173-3°,  $n_D^{20}$  1.4424,  $d_4^{20}$  1.2034; 71% *di-Et ester analog*,  $b_p$  179-80°, 1.4355, 1.1278; 47%  $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CH}(\text{CO}_2\text{Et})_2$ ,  $b_p$  144-10, 1.0750; 51%  $(\text{EtO})_2\text{P}(\text{S})\text{CH}_2\text{CH}(\text{CO}_2\text{Et})_2$ ,  $b_p$  180-3°, 1.4570, 1.1128. Slow addn. of  $\text{EtONa}$  in  $\text{EtOH}$  to 10 g.  $\text{PhCH:CAc}_2$  and 11 g.  $(\text{EtO})_2\text{POH}$  gave after a long induction period a rapid exothermic reaction which yielded 4.2 g.  $\text{PhCH}(\text{CH}_2\text{Ac})\text{P}(\text{O})(\text{OEt})_2$  (II),  $b_p$  190-1°, 1.5005, 1.1294, formed by evident decarboxylation of the expected product. Similar reactions but using *di-n-Bu* instead of *di-Et* gave after

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Distr: 4E4j/4E3d/4E2o(j)

A. N. Pudovik + t. M. Moshkina et al.

EtONa in 20-30 ml. abs. EtOH with 0.07 mole  $\text{CO}(\text{NH}_2)_2$  or  $\text{CS}(\text{NH}_2)_2$  and refluxed 6-7 hrs. gave after soln. in  $\text{H}_2\text{O}$  and acidification the corresponding phosphonobarbituric acids. Thus were prep'd. in 60-70% yields:  $(\text{MeO})_2\text{P}(\text{O})\cdot\text{CH}_2\text{CH}(\text{CONH})_2\text{CO}$ , m. 97°; di-Et ester, m. 100°; di-Bu ester, m. 109°;  $(\text{EtO})_2\text{P}(\text{S})\text{CH}_2\text{CH}(\text{CONH})_2\text{CO}$ , m. 98-100°;  $(\text{MeO})_2\text{P}(\text{O})\text{CH}_2\text{CH}(\text{CONH})_2\text{CS}$ , m. 161°; di-Et ester, m. 162-3°; di-Bu ester, m. 168°;  $(\text{EtO})_2\text{P}(\text{S})\text{CH}_2\text{CH}(\text{CONH})_2\text{CS}$ , m. 163-4°;  $(\text{MeO})_2\text{P}(\text{O})\text{CHMeCH}(\text{CONH})_2\text{CO}$ , m. 105°;  $(\text{EtO})_2\text{P}(\text{O})\text{CHMeCH}(\text{CONH})_2\text{CO}$ , m. 107°;  $(\text{BuO})_2\text{P}(\text{O})\text{CHMeCH}(\text{CONH})_2\text{CO}$ , m. 110°;  $(\text{EtO})_2\text{P}(\text{S})\text{CHMeCH}(\text{CONH})_2\text{CO}$ , m. 144°;  $(\text{MeO})_2\text{P}(\text{O})\text{CHMeCH}(\text{CONH})_2\text{CS}$ , m. 177°;  $(\text{EtO})_2\text{P}(\text{O})\text{CHPhCH}(\text{CONH})_2\text{CO}$ , m. 109°;  $(\text{EtO})_2\text{P}(\text{S})\text{CHPhCH}(\text{CONH})_2\text{CO}$ , m. 110°;  $(\text{EtO})_2\text{P}(\text{O})\text{CHPhCH}(\text{CONH})_2\text{CS}$ , m. 178°;  $(\text{EtO})_2\text{P}(\text{S})\text{CHPhCH}(\text{CONH})_2\text{CS}$ , m. 179°. Prepn. of  $(\text{RO})_2\text{P}(\text{O})\text{CH}(\text{CO}_2\text{R})_2$  was accomplished by 3 different routes, all of which giving the same product; hence the Arbuzov reaction (cf. A. and Kamal, C.A. 42, 4523g) is normal with halomalononic esters and the supposition about its abnormality made by Allen and Johnson (C.A. 50, 3272k) is incorrect. Heating 16.6 g.  $(\text{EtO})_2\text{P}$  and 23.9 g.  $\text{BrCH}(\text{CO}_2\text{Et})_2$  3 hrs. on a steam bath gave 17 g.  $(\text{EtO})_2\text{P}(\text{O})\text{CH}(\text{CO}_2\text{Et})_2$ , b<sub>18</sub> 160-1°, 1.4420, 1.1660; similarly  $\text{ClCH}(\text{CO}_2\text{Et})_2$  and  $(\text{EtO})_2\text{P}$  after 3 hrs. on a steam bath gave the same product,  $(\text{EtO})_2\text{P}(\text{O})\text{CH}(\text{CO}_2\text{Et})_2$ , b<sub>18</sub> 160-1°, 1.4416, 1.1644; reaction of 10 g.  $(\text{EtO})_2\text{POCl}$  with Na deriv. from 1.3 g. Na and 9.2 g.  $\text{CH}_2(\text{CO}_2\text{Et})_2$  in  $\text{Et}_2\text{O}$  gave after 10 hrs. refluxing 5 g.  $(\text{EtO})_2\text{P}(\text{O})\text{CH}(\text{CO}_2\text{Et})_2$ , b<sub>18</sub> 159-60°, n<sub>D</sub><sup>20</sup> 1.4458. This (1.4 g.) and 2 g.  $\text{CO}(\text{NH}_2)_2$  as above gave 0.46 g.  $(\text{EtO})_2\text{P}(\text{O})\text{CH}$

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*A. N. Pudovik & T. M. Mashkina*

(CONH)<sub>2</sub>CO, m. 97°; the phosphonomalonate from an alternate route gave the same product, m. 98°. To Na deriv. from 2 g. Na and 10 g. CH<sub>3</sub>Ac<sub>2</sub> was added 15 g. (EtO)<sub>2</sub>P(O)Cl in Et<sub>2</sub>O and after refluxing 12 hrs. the filtrate gave 5.3 g. (EtO)<sub>2</sub>P(O)CHAc<sub>2</sub>, b<sub>p</sub> 161-2°, n<sub>D</sub><sup>20</sup> 1.4328. Refluxing 2 g. of this with 3 g. CO(NH<sub>2</sub>)<sub>2</sub> in dioxane and dry EtONa 10 hrs., dissolving the ppt. in H<sub>2</sub>O, acidifying with HCl and

concg. gave 0.4 g. (EtO)<sub>2</sub>P(O)C(CMe)NH.CO.N:CM<sub>2</sub>, m. 115-17° (EtOH). XVIII. Reaction of incomplete esters of acids of phosphorus with  $\alpha,\beta$ -unsaturated cyclic ketones and cyclohexenyl acetate. A. N. Pudovik and I. V. Kononova. *Ibid.* 1617-21. Addn. of (RO)<sub>2</sub>POH or (RO)<sub>2</sub>PSH to 2-cyclohexenone and its methylated analogs occurs readily after addn. of catalytic amts. of RONA; after termination of the exothermic reaction, the mixts. were neutralized with AcOH and distd., yielding the following esters: di-Et 3-oxocyclohexylphosphonate, 54%, b<sub>p</sub> 170°, n<sub>D</sub><sup>20</sup> 1.2840, d<sub>4</sub> 1.1210; di-Me ester, 48%, b<sub>p</sub> 160°, 1.4723, 1.2131; di-Et 3-oxocyclohexylthiophosphonate, 57%, b<sub>p</sub> 182°, 1.4998, 1.1307; di-Me 3-oxo-2-methylcyclohexylphosphonate, 68%, b<sub>p</sub> 162°, m. 98°; di-Et ester, 50%, b<sub>p</sub> 168°, 1.4612, 1.1007; di-Et 3-oxo-2-methylcyclohexylthiophosphonate, 60%, b<sub>p</sub> 165°, 1.4936, 1.1099; di-Me 3-oxo-1-methylcyclohexylphosphonate, 47%, b<sub>p</sub> 162°, 1.4721, 1.1801; di-Et ester, 54%, b<sub>p</sub> 187°, 1.4653, 1.1130; di-Et 3-oxo-1-methylcyclohexylthiophosphonate, 53%, b<sub>p</sub> 172°, 1.4950, 1.1182; di-Et 3-oxo-2,5-dimethylcyclohexylphosphonate, 68%, b<sub>p</sub> 162°, 1.4810, 1.0810; di-Me ester, 60%, b<sub>p</sub> 165°, 1.4750, 1.1499; di-Et 3-oxo-2,5-dimethylcyclohexylthiophosphonate, 66%, b<sub>p</sub> 173°, 1.4921, 1.0940; di-Bu 3-oxo-2,5-dimethylcyclohexylphosphonate, 59%, b<sub>p</sub> 196°, 1.4580, 1.0189; di-Et 3-oxo-2,5,5-trimethylcyclohexylphosphonate, 60%, b<sub>p</sub> 167°, 1.4641,

*A.N. Pudovik + T.M. Mashkina*

1.0710. Addn. of satd.  $\text{EtONa-EtOH}$  dropwise to 10.5 g.  $(\text{EtO})_2\text{POH}$  and 10.5 g. 1-cyclohexenyl acetate gave a very exothermic reaction which resulted, after cooling and acidification, in isolation of 5 g. cyclohexanone and 13 g.  $\text{MeC}(\text{OAc})(\text{PO}(\text{OEt}))_2$  (I), b: 174-5.5°, d<sub>4</sub> 1.1511, n<sub>D</sub> 1.4308; the latter product formed along with 2-methylcyclohexanone in a similar reaction of 2-methylcyclohexenyl acetate. To 19 g.  $\text{AcP}(\text{O})(\text{OEt})_2$  and 15 g.  $(\text{EtO})_2\text{POH}$  was added dropwise  $\text{EtONa-EtOH}$  and after the strongly exothermic reaction there formed 20 g. I, b.p. 180°, d<sub>4</sub> 1.1535, n<sub>D</sub> 1.4300; I heated with  $\text{BzCl}$  in  $\text{PhNMe}_2$  1 hr. at 60° was benzoylated to the extent of but 5.8%. Reaction of 6.3 g. 1-cyclohexenyl acetate with 7 g.  $(\text{EtO})_2\text{PSH}$  in the presence of  $\text{EtONa}$  as above gave 3 g. cyclohexanone and 9.8 g. product, b. 169°, 1.1421, 1.4710, identified as  $\text{MeC}(\text{OAc})(\text{PS}(\text{OEt}))_2$ . The latter, b. 168-70°, 1.1410, 1.4710, also formed along with 2-methylcyclohexanone in a similar reaction of 2-methylcyclohexenyl acetate. G. M. F.

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~~PUDVIK, A.N.~~; KOROZALOV, I.V.

New method for the synthesis of phosphinic and thiophosphinic acids.  
Part 28: Reaction of incomplete phosphorous acid esters with  
 $\alpha, \beta$ -unsaturated cyclic ketones and cyclohexenol acetate. Zhur.  
ob.khim. 27 no.6:1617-1621 Je '57. (1957 16:3)

I.Kazanskiy gosudarstvennyy universitet.  
(Phosphorous acid) (Cyclohexenol) (Ketones)

PUDOVIK, A. N.

Distr: 4E43/4B20(1)

Anomalous reaction of  $\alpha$ -halo ketones with esters of phosphorous acid. V. Reactions of halogen derivatives of methyl ketone and acetophenone with triethyl phosphite. A. N. Pudovik and L. G. Biktimirova (State Univ., Moscow). *Zhur. Obshchei Khim.* 27, 1708-12 (1957); cf. C.A. 50, 84884; 51, 18276. Haloketones having the halogen on a secondary C atom are more prone to the anomalous course of reaction with  $(RO)_3P$  than halo ketones with halogen on the primary C atom. To 28.4 g.  $MeCOCHClMe$  preheated to 90-100° was added 43.4 g.  $(EtO)_3P$  and the mixt. gradually heated to 120° giving  $EtCl$  and 35.3 g.  $(EtO)_3P(O)OCMe$ : CHMe (I),  $b_p$  110-11.5°,  $d_4$  1.0598,  $n_D^{20}$  1.4274; this heated with  $EtONa-EtOH$  gave  $MeEtCO$  and  $(EtO)_3PO$ ; ozonolysis of the unsatd. ester gave  $AcH$ . Heating 49.8 g.  $MeCOCHBrMe$  and 58.6 g.  $(EtO)_3P$  in dry  $Et_2O$  gave after 2.5 hrs. refluxing 36 g. I;  $b_p$  111.6-12°, 1.0578, 1.4272, and 5 g.  $AcCHMeP(O)(OEt)_2$  (II),  $b_p$  123-5°, 1.4. If the phosphite was added to the bromo ketone preheated to 110° and the mixt. heated 4 hrs. at 130-40° there was formed 37.9 g. I and 8.8 g. II. Heating I or II at 100° in  $H_2O$ , followed by periodic titrations, showed that I is sapond. more rapidly than II; in 20 hrs. 39.8% I was hydrolyzed, while only 14% II was attacked. To 20 g.  $(EtO)_3P$  preheated to 120° was added 14.6 g. 3-bromocyclohexanone yielding 3.1 g.  $(EtO)_3POH$  and 13.4 g. di-*Et* cyclohexenyl phosphate,  $b_p$  144°, 1.1033, 1.4518; the same products formed on addn. of bromocyclohexanone to refluxing  $(EtO)_3P$ . Heating the ester with  $EtONa-EtOH$  gave cyclohexanone and  $(EtO)_3PO$ , thus confirming the structure of the former. Addn. of 38.5 g.  $(EtO)_3P$  to 49 g.  $MeCOCHBrMe$  at 20-30° gave on distn. some  $EtBr$  and

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2 May  
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PUDOVNIK, A. N.; BIKTIMIROVA, L. G.

22.8 g.  $(EtO)_2P(O)OCMe:CBzMe$ , b.p. 147-8° (some decompn.), 1.3481, 1.4655; passage of Cl into this ester in  $CCl_4$  with ice cooling gave  $(EtO)_2P(O)OCMeClCBzMe$ , b.p. 164-5°, 1.4677, 1.4760. Addn. of 32.7 g.  $(EtO)_2P$  to 55.4 g.  $BrCH_2COCHBr_2$  at 60° gave 7.1 g.  $(EtO)_2P(O)OCMe:CBz$ , b.p. 145-8°, 1.6340, 1.4935 (with much decompn.). Addn. of 44 g.  $(EtO)_2P$  to 50 g.  $PhCOCH_2CH_3$  at 20-30° gave 71 g.  $(EtO)_2P(O)OCPh:CHCl$ , b.p. 139-40°, 1.2353, 1.5170, which chlorinated in  $CCl_4$  with ice cooling to  $(EtO)_2P(O)OCPh:ClCHClCH_3$ , b.p. 162-3°, 1.3487, 1.5149. Addn. of 39 g.  $(EtO)_2P$  to 47.6 g.  $PhCOCCl_2$  at 20-30° gave 53.8%  $(EtO)_2P(O)OCPh:CCH_3$ , b.p. 145-6°, 1.8945, 1.5200.  $(EtO)_2P$  reacted with haloketones. On heating dichloro- and dibromobenzylideneacetone, 3,4-dichloro-2-hexanone, and 3,4-dichloro-4-methyl-2-pentanone to 100-50°, the products could not be distd. or isolated owing to decompn. and tar formation.

G. M. Kosolapoff

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PUDOVIK, A-N.

Distr: 4E4J/4E2c(j)/4E3d

V Anomalous reaction of  $\alpha$ -halo ketones with esters of phosphorous acid. VI. Reaction of esters of phosphorous acid with halides of halosubstituted carboxylic acids. A. N. Pudovik and L. G. Bikturova (State Univ., Kazan). *Zhur. Obshchei Khim.* 27, 2104-8 (1957); *Ch. S.S.S.R.* 32, 3714c. To  $(RO)_3P$  was added the desired  $KOOC-R$  in which R is a halogen-bearing radical. The reactions were exothermic, requiring cooling. After termination of evolution of alkyl halide, the product were distd. Reaction of  $(MeO)_3P$  with  $ClCH_2COCl$ , with heating 0.5 hr. at  $100^\circ$  gave 84% product identified as  $(MeO)_3P(O)OC(ClCH_2)P(O)(OMe)_3$ ,  $b_p$   $141^\circ$ ,  $d_4$  1.3214,  $n_D^{20}$  1.4420; similar reaction with  $(EtO)_3P$  gave the *tetra-Et* analog, 86.4%,  $b_p$   $125-6^\circ$ , 1.1827, 1.4396. The same reaction run in  $Et_2O$  gave a low yield. Ozonolysis of the products in  $CCl_4$  gave  $CH_3CO$ , thus confirming the structure.  $(MeO)_3P$  and  $Me_2CBrCOBr$  similarly gave 92.3% product, identified as  $Me_2C: C[PO(OMe)_3]OP(O)(OMe)_3$ ,  $b_p$   $131-2^\circ$ , 1.2756, 1.4680, while  $(EtO)_3P$  gave 90% corresponding *tetra-Et* ester,  $b_p$   $134-5^\circ$ , 1.1602, 1.4503.  $(MeO)_3P$  and  $CCl_3COCl$  at below  $30^\circ$  gave 78.3%  $CCl_3: C[PO(OMe)_3]OP(O)(OMe)_3$ ,  $b_p$   $134-5^\circ$ , 1.4901, 1.4770, while the  $(EtO)_3P$  reaction gave 78.6% *tetra-Et* ester,  $b_p$   $132-3^\circ$ , 1.3219, 1.4600. If the last reaction is run in  $Et_2O$ , there was obtained the above *tetra-Et* ester and a somewhat greater amt. of  $CCl_3COP(O)(OEt)_3$ ,  $b_p$   $95^\circ$ , 1.3916, 1.4632, which is evidently the intermediate in the formation of the di-phosphorus esters. The phosphonate is formed also if the phosphite is used in less than the theoretical amt. for the reaction with the acyl halide. Reaction of  $(EtO)_3P$  with  $MeCHBrCOBr$  at  $100^\circ$  (final temp.) gave 78.0%  $MeCH: C[PO(OEt)_3]OP(O)(OEt)_3$ ,  $b_p$   $128-9^\circ$ , 1.1690, 1.4450. Thus, halosubstituted acyl halides react with phosphites predominantly by the anomalous route. G. M. Kosolapoff

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PUDOVIK, A.N.

Glorious anniversary on the eightieth birthday and fiftieth  
anniversary of scientific activity of Academician A.E. Arbuzov.  
Zhur. ob. khim. 27 no.9:2312-2328 S '57. (MIRA 11:3)  
(Arbuzov, A.E. 1877-)

*Pudovik, A. N.*

<sup>7</sup> Addition of alcohols to isoprene oxide. A. N. Pudovik and S. G. Denislamova (State Univ., Kazan, Kazan. Obshch. Khim. 27, 2363-7(1957); cf. Petrov, C.A. 43, 8167c; Kadesch, C.A. 40, 1450<sup>9</sup>.—To 185 ml. dry MeOH was added 0.15 ml. BF<sub>3</sub>·Et<sub>2</sub>O followed, with cooling, by 34 g. 1,2-epoxy-2-methyl-3-butene (I) and after 4 hrs. on a steam bath the mixt. gave 13 g. 2-methoxy-2-methyl-3-buten-1-ol (II), b<sub>10</sub> 75-8°, n<sub>D</sub><sup>20</sup> 1.4390, d<sub>4</sub> 0.9457, and 4.5 g. mixed products, b<sub>10</sub> 98-170°. II with BzCl and PhNMe<sub>2</sub> in 1 hr. at 60° gave 36% Bz deriv. I (34 g.) added to 1 g. Na in 200 ml. dry MeOH and heated 10 hrs. on a steam bath gave 15.6 g. 1-methoxy-2-methyl-3-buten-2-ol, b<sub>10</sub> 62.5-3°, n<sub>D</sub><sup>20</sup> 1.4285, d<sub>4</sub> 0.9193, and 1.7 g. II. Similarly BF<sub>3</sub>·Et<sub>2</sub>O, I, and EtOH gave 2-ethoxy-2-methyl-3-buten-1-ol, b<sub>10</sub> 52.3-3.3°, 1.4380, 0.9227, while a reaction with EtOH contg. some Na gave but small amt. of this product, and much 2-methyl-1-ethoxy-3-buten-2-ol, b<sub>10</sub> 45-6°, 1.4720, 0.8971. Similarly, I and BuOH in presence of BF<sub>3</sub>·Et<sub>2</sub>O gave mainly 2-butoxy-3-methyl-3-buten-1-ol (III), b<sub>10</sub> 80-1°, 1.4390, 0.9030, and a product of further addn., C<sub>11</sub>H<sub>22</sub>O<sub>2</sub>, b<sub>10</sub> 124-5°, 1.4550, 0.9360; I and BuOH contg. a little Na gave mostly 1-butoxy-2-methyl-3-buten-2-ol, b<sub>10</sub> 69.5-70.5°, 1.4303, 0.8777, and a little III. I and iso-BuOH with BF<sub>3</sub>·Et<sub>2</sub>O gave 2-isobutoxy-2-methyl-3-buten-1-ol, b<sub>10</sub> 67-8°, 1.4380, 0.9001, while iso-BuOH-iso-BuONa treatment gave mainly 1-isobutoxy-2-methyl-3-buten-2-ol, b<sub>10</sub> 58.5-9°, 1.4270, 0.8730, and a little of the above isomer. Allyl alc. and I in presence of BF<sub>3</sub>·Et<sub>2</sub>O gave mainly 2-allyloxy-2-methyl-3-buten-1-ol, b<sub>10</sub> 77-8°, 1.4530, 0.9392, while reaction with ROH·RONa gave mainly 1-allyloxy-2-methyl-3-buten-2-ol, b<sub>10</sub> 68.5-9.5°, 1.4455, 0.9164, and a little of the above isomer. G. M. K.

Distr: 4E2c(j)/4E4j/4E3d

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PUDOVIK, A.N.; SHCHELKI~~NA~~<sup>NA</sup>, L.P.; BASHIROVA, L.A.

Substitution reaction of phosphoacetic ester and phosphoacetone.  
Zhur. ob. khim. 27 no.9:2367-2371 S '57. (MIRA 11:3)

1. Kazanskiy gosudarstvennyy universitet.  
(Acetic acid) (Acetone)

PUDOVIK, A.N.; SHERGINA, I.V.

Allyl regrouping. Part 19: The reaction of magnesium organic compounds and sodium diethylphosphorate with isomeric isoprene hydrochloride and methoxychloroisohexanes. Zhur.ob.khim. 27 no.10: 2750-2755 0 '57. (MIRA 11:4)

1. Kazanskiy gosudarstvennyy universitet.  
(Magnesium--Organic compounds)  
(Isoprene) (Hexane)

PU DVPK, A. N.

Dealkylation of isomeric tributyl phosphites by hydro-  
 gen chloride. A. N. Pudovik (State Univ. Kazan).  
 Zhur, Obshch. Khim. 27, 2765-66 (1957); J. C.A. 47,  
 3226g; Abramov and Karp, C.A. 49, 13687c. It is now  
 shown that (RO)<sub>3</sub>P are intermediate products in the reaction  
 of PCl<sub>5</sub> with isomeric butenols; the initial dealkylation of  
 these occurs along the lines of Arbuzov rearrangement by the  
 attack of HCl. Further attack by HCl may pursue S<sub>N</sub>1 or  
 S<sub>N</sub>2 routes. Since (RO)<sub>3</sub>POH are attacked by dry HCl at  
 -10° only very slowly if the radicals in the esters are pri-  
 mary and secondary, the rapid dealkylation of crotyl and  
 diisobutenyl esters may be explained by direct action of HCl  
 on the quinquivalent form of the ester through 4-center re-  
 action at the PO group with electron supply provided by in-  
 duction of alkyl groups aiding the reaction. Crotyl alc.  
 (84.8 g.), 109 g. PhNMe<sub>2</sub>, and 41.3 g. PCl<sub>5</sub> in Et<sub>2</sub>O gave 45.6  
 g. (MeCH:CHCH<sub>2</sub>O)<sub>3</sub>P, b<sub>1</sub> 98-9°, d<sub>4</sub> 0.9757, n<sub>D</sub> 1.4680;  
 this (10 g.) treated with dry HCl at -10° gave 6.5 g. mixed  
 chlorobutenes (86% 1-chloro-2-butene and 14% 2-chloro-3-  
 butene) and 3.2 g. H<sub>3</sub>PO<sub>4</sub>. Addn. of 37 g. PCl<sub>5</sub> to 50 g.  
 crotyl alc. at -15° gave after 0.5 hr. stirring and quenching  
 in ice 59.5 g. mixed chlorobutenes of the same compn. as  
 above. Similarly, PCl<sub>5</sub> and MeCH(OH)CH:CH<sub>2</sub> gave the  
 same mixt. of chlorides. PCl<sub>5</sub> with BuOH under these con-  
 ditions gave 84% (BuO)<sub>3</sub>PHO, while allyl alc. gave 42%  
 (CH<sub>2</sub>:CHCH<sub>2</sub>O)<sub>3</sub>PHO (on distn. the residue tends to ex-

Distr: 4E4j/4E2c(j)/4E3d

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A. N. Pudovik

plode violently if heated unduly). Passage of dry HCl into (BuO)<sub>3</sub>P at -10° and stirring 0.5 hr. gave 1 mole BuCl and (BuO)<sub>2</sub>PHO. Similarly, (CH<sub>3</sub>:CHCH<sub>2</sub>O)<sub>3</sub>P and HCl gave allyl chloride and (RO)<sub>2</sub>PHO, b. 97-8°, n<sub>D</sub><sup>20</sup> 1.4430, with much residue. HCl with (CH<sub>3</sub>:CHCHMeO)<sub>3</sub>P gave H<sub>3</sub>PO<sub>4</sub> and mixed butenyl chlorides (50-53% 1-chloro-2-butene and 47-50% 2-chloro-3-butene). Keeping (RO)<sub>3</sub>P in Et<sub>2</sub>O in the presence of dry HCl at room temp. and following the reaction by periodic analysis for labile Cl showed that in 8 days the Bu ester lost 0.96, allyl ester lost 1.7, crotyl ester lost 2.2, and methallyl ester lost 2.2 ester groups.

G. M. Kosolapoff

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2 May  
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AUTHORS: Pudovik, A. N., Konovalova, I. V.

79-28-5-16/69

TITLE: A New Method of Synthesis of the Esters of Phosphinic and Thiophosphinic Acids (Novyy metod sinteza efirov fosfinovykh i tiofosfinovykh kislot) XXIX. Addition of Dialkylphosphorous Acids to the Esters of the Vinyl-Alkrylic- and Sorbic Acid, as Well as to the 3,5-Heptadienone-2 (XXIX. Prisoyedineniye dialkilfosforistykh kislot k efiram vinilakrilovoy, sorbinovoy kislot i 3,5-heptadiyenonu-2)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 5, pp. 1208 - 1211 (USSR)

ABSTRACT: In continuation of earlier papers (Reference 1) the authors describe the results of the addition reactions of dimethylphosphorous and diethylphosphorous acids to the esters of the  $\beta$ -vinylakrylic- and sorbic acids, to 3,5-heptadienone-2, and to the diethylester of butadienephosphinic acid. Alkali alcoholates were used as catalysts in these reactions. All reactions take a vigorous course and are accompanied by a considerable heat effect. Products of the addition of one or two molecules were obtained as result of the addition of diethylphosphorous acid (in excess) to the ethylester of  $\beta$ -vinylakrylic

Card 1/3

79-28-5-16/69

A New Method of Synthesis of the Esters of Phosphinic and Thiophosphinic Acids. XXIX. Addition of Dialkylphosphorous Acids to the Esters of the Vinyl-Alkrylic- and Sorbic Acid, as Well as to the 3,5-Heptadienone-2

acid, namely: the ethylesters of 4-(diethylphosphonium)butene-2-carboxylic acid (formula I of scheme 1) and 2,4-di-(diethylphosphonium)butanecarboxylic acid (II). The structure of (I) was hardened by ozonization and decomposition of the ozonides. The binding of diethylphosphorous acid to the ethylsorbinate also leads to the formation of two products (III and IV of scheme 2). Product (III) contains a double bond and represents a product of the addition of a molecule of diethylphosphorous acid. From the obtained ozonization results could be concluded that (III) represents mainly a  $\gamma,\delta$ -product of the addition, which contains the forms  $\alpha,\beta$ - or  $\alpha,\delta$ -(or both together). Product (IV) does not contain a double bond and represents an addition product of two molecules of diethylphosphorous acid to 3,5-ethylsorbinate. In the case of the addition of diethylphosphorous acid to 3,5-heptadienone-2, compound (V) with a double bond resulted. By ozonization

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79-28-5-16/69

A New Method of Synthesis of the Esters of Phosphinic and Thiophosphinic Acids. XXIX. Addition of Dialkylphosphorous Acids to the Esters of the Vinyl-Alkrylic-and Sorbic Acid, as Well as to the 3,5-Heptadienone-2

and further treatment of the ozonides this formula was proved.  
There are 2 references, which are Soviet.

ASSOCIATION: Kazanskiy gosudarstvennyy universitet (Kazan' State University)

SUBMITTED: May 3, 1957

Card 3/3

AUTHORS: Pudovik, A. N., Biktimirova. L. G. SOV/79-28-6-11/63

TITLE: The Anomalous Reaction of  $\alpha$ -Halogen Ketones With Esters of Phosphorous Acid (Anomal'naya reaktsiya  $\alpha$ -galoidketonov s efirami fosforistoy kisloty) VII. The Reactions of the Esters of Phosphorous Acid With the Chlorine Derivatives of  $\beta$ -Diketones (VII. Reaktsii efirov fosforistoy kisloty s khlorproizvodnymi  $\beta$ -diketonov)

PERIODICAL: Zhurnal obshchey khimii, 1953, Vol. 28, Nr 6, pp. 1496-1500 (USSR)

ABSTRACT: In the present paper the authors investigated the reactions of the chlorine- and dichlorine-substituted compounds of acetyl-benzoyl-acetone, dibenzoylmethane and dimedone with various phosphites. As was to be predicted from earlier results obtained unsaturated esters of phosphoric acid occurred as intermediate or final products in all these reactions. The reactions of chloro- and dichloroacetylacetone with trimethyl- and tri-n-butylphosphite take place completely anomalously: in yields of 60 - 80 % (1-methylbutene-1-on-3-yl)-dialkyl-, or (1-methyl-2-chlorobutene-1-on-3-yl)-dialkyl-ester of phosphoric acid respectively were obtained. (See

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SOV79-28-6-11/63

The Anomalous Reaction of  $\alpha$ -Halogen Ketones With Esters of Phosphorous  
 Acid. VII. The Reactions of the Esters of Phosphorous Acid With the Chlorine  
 Derivatives of  $\beta$ -Diketones

formulae I - IV of the table). The presence of double bonds in these compounds was proved by bromination according to Mak-Ilineyu. In the case of careful saponification of compound (I) of the table acetylacetone was obtained. It is of interest that after two months this compound turned brown at room temperature and smelled like acetylacetone. In fact 10 % of the latter could be separated in the distillation, the residual representing the unchanged product. In carrying out the reactions of chlorobenzoylacetone with trimethyl- and triethylphosphite (yield 70 - 80 %) the (1-phenylbutene-1-on-3-yl)-dimethyl- and (1-phenylbutene-1-on-3-yl)-diethyl-ester of phosphoric acid were obtained (formula V and VI of the table). Also in this case the double bonds were determined by bromination and on storing this compound a small amount of benzoylacetone crystallized out, too. Thus all these reactions take an anomalous course and not one according to the regrouping as mentioned by Arbuzov (Ref 1). Some of these unsaturated esters of phosphoric acid, especially those with

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Sov/ 79-28-6-11/63

The Anomalous Reaction of  $\alpha$ -Halogen Ketones With Esters of Phosphorous Acid. VII. The Reactions of the Esters of Phosphorous Acid With the Chlorine Derivatives of  $\beta$ -Diketones

the phenyl- and cyclohexene radical split up on heating under the formation of a  $\beta$ -dicarbonyl compound. There are 3 figures, 1 table, and 4 references, 3 of which are Soviet.

ASSOCIATION: Kazanskiy gosudarstvennyy universitet  
(Kazan' State University)

SUBMITTED: May 3, 1957

1. Ketones--Chemical reactions    2. Phosphoric acids--Chemical reactions

Card 3/3

PUDOVIK, A.N.; CHEBOTAREVA, E.G.

Anomalous reaction of phosphites with  $\alpha$ -halogenketones. Part 8:  
Reactions of mixed phosphites with chloro and dichloro acetone.  
Zhur.ob.khim. 28 no.9:2492-2496 S '58. (MIRA 11:11)

1. Kazanskiy gosudarstvennyy universitet.  
(Acetone) (Phosphites)

FUDOVIK, A.N.; ALADZHEVA, I.M.

Addition of ammonia and amines to isoprene oxide. Zhur.ob.khim.  
28 no.9:2497-2500 S '58. (MIRA 11:11)

1. Kazanskiy gosudarstvennyy universitet.  
(Ammonia) (Amines) (Isoprene)

5(3)

AUTHORS: Kukhtin, V. A., Iudovik, A. N. (Kazan') SOV/74-26-1-5/5

TITLE: Several New Types of Arbuzov Rearrangements  
(nekotoryye novyye vidy peregruppirovki Arbuzova)

PERIODICAL: Dopekhi khimii, 1959, Vol 28, Nr 1, pp 96-116 (USSR)

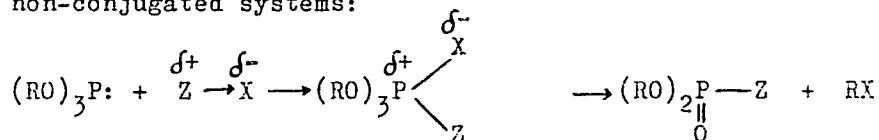
ABSTRACT: The reaction listed in the scientific publications as the rearrangement of Arbuzov was discovered in 1905 by A. Ye. Arbuzov. At present it represents one of the most important methods for synthesizing esters of phosphinic acids and their derivatives. The authors of this paper give a review of the most recent research work on this reaction and on broadening its application. In summary it may be said that the chemistry of trivalent phosphorous has entered a new phase of development. The basic type of Arbuzov rearrangement has been found to be characteristic of a whole new series of reactions of phosphites with various reagents. The current understanding of the Arbuzov reaction, which has been concerned only with the effect of alkyl halogens on the esters of trivalent phosphorous (Refs 86, 87), must be expanded on the basis of existent experimental material. The transformation of esters of trivalent phosphorous to derivatives of pentavalent

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Several New Types of Arbuzov Rearrangements

SOV/74-28-1-5/5

phosphorous, which takes place using saturated as well as - unsaturated electrophilic reagents with and without halogen atoms, should be considered a part of the Arbuzov rearrangement, since it is accompanied by the formation of a new P-El bond (El= C, N, O, S, and others). The nature of the rearrangement consists in the primary attack on the especially electrophilic part of the molecule by the nucleophilic phosphorous atom to form, usually, an intermediate form. This form then splits off the ester radical of the phosphite through the effect of the especially electronegative part of the associated reagent to form the endproduct, in which the P=O bond has formed. There are at least three basic types of Arbuzov rearrangements: 1. Rearrangement under the effect of non-conjugated systems:



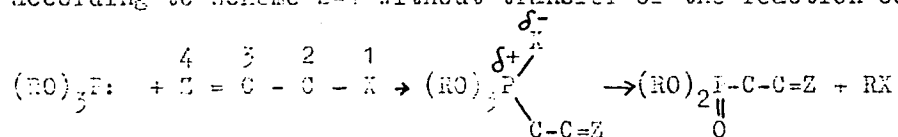
Card 2/4



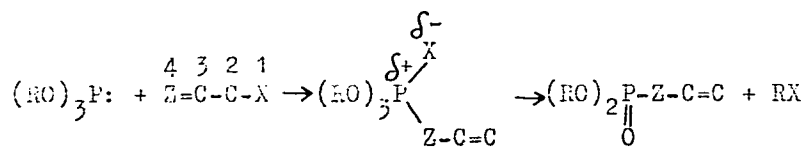
Several New Types of Arbuzov Rearrangements

SOV/74-28-1-5/5

2. Rearrangement under the effect of  $\sigma$ ,  $\pi$ -conjugated systems. This type can occur in the following directions. a) Reaction according to scheme 2-1 without transfer of the reaction center:



b) Reaction according to scheme 4-1 or with transfer of the reaction center:

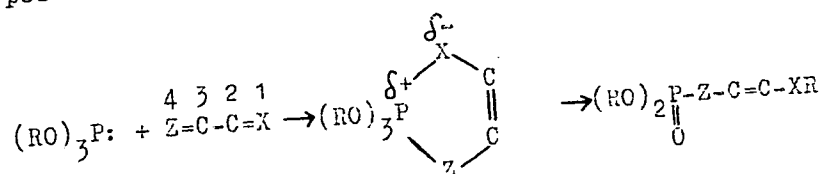


3. Rearrangement involving  $\pi$ ,  $\pi$ -conjugated systems apparently occurs always by scheme 4-1 with transfer of the reaction center:

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Several New Types of Arbuzov Rearrangements

SOV/74-26-1-5/5



These three basic types apparently cannot include all the various cases of this reaction. Complicated electron systems with a mixed conjugation (e.g. halogen acrylates, lactones, and several others) exhibit specific behavior in the reaction. Reagents which tend to form free radicals can be included in the Arbuzov rearrangement under certain conditions, according to the radical-chain mechanism, which differs from all the others mentioned above. Esters of trivalent phosphorous have not only the tendency to undergo the Arbuzov rearrangement, but they can also undergo numerous other reactions. Further research work on the rearrangement of Arbuzov promises to yield new and interesting results. There are 87 references, 57 of which are Soviet.

Card 4/4

USCOMM-DC-60841

AUTHORS: Pudovik, A. N., Platonova, R. N. SOV/79-29-2-31/71

TITLE: On the Reaction of Phosgene and Oxalyl Chloride With Esters of Phosphorous Acid (O reaktsii fosgena i khloristogo oksalila s efirami fosforistoy kisloty)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 2, pp 507-510 (USSR)

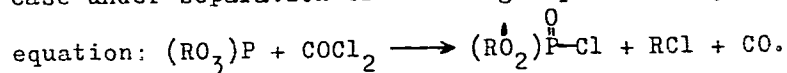
ABSTRACT: In connection with previous investigations concerning reactions of phosphites with halogen anhydrides of  $\alpha$ -halogen-substituted carboxylic acids it was a matter of course that the authors would carry out the reactions of phosphites with halogen anhydrides of dibasic acids. The results they obtained in the reactions of complete phosphites with phosgene were in contrast to those described by M. I. Kabachnik and P. A. Rossiyskaya (Ref 6). On the reaction of phosgene with triethyl phosphite the authors obtained the chloric anhydride (IV), which, together with ethyl alcohol in the presence of pyridine or sodium ethylate, permitted substitution of the ethoxy group for chlorine, while ester (V) was formed simultaneously. According to the data obtained by Kabachnik's and Rossiyskaya's investigation, the ethyl ester of diethyl phosphonoformic acid

Card 1/3

On the Reaction of Phosgene and Oxalyl Chloride  
With Esters of Phosphorous Acid

SOV/79-29-2-31/71

$((C_2H_5O)_2\overset{O}{P}-COOC_2H_5)$  ought to be formed. This ester obtained by A. Ye. Arbuzov (Ref 7) by action (VI) of chlorocarbonic ester on triethyl phosphite was not identical with compound (VI). For this reason, the authors repeated its synthesis according to reference 7. The constants of the products synthesized are listed in table 1. It results from them that compound (V) does not agree with (VI) but represents a triethyl phosphate. After further experiments of identification, i.e., due to the reaction of phosgene with the methyl, ethyl, and butyl ester of phosphorous acid, and 2) after the synthesis of some chloric anhydrides of dialkyl phosphoric acids by the action of chlorine on dialkyl phosphorous acids (Table 2), in the course of which the reaction products were identical in both cases and represented chloric anhydrides of dialkyl phosphoric acid, the following results were obtained: the reactions of phosgene with complete esters of phosphorous acid take place in any case under separation of the CO group according to this



Card 2/3

On the Reaction of Phosgene and Oxalyl Chloride  
With Esters of Phosphorous Acid

SOV/79-29-2-31/71

The reaction of the chloric anhydride of oxalic acid with trimethyl and triethyl phosphite also takes place in the same way, yet the respective yields are smaller (last-mentioned Scheme). There are 2 tables and 9 references, 7 of which are Soviet.

ASSOCIATION: Kazanskiy gosudarstvennyy universitet (Kazan' State University)

SUBMITTED: December 26, 1957

Card 3/3

SOV/79-29-4-38/77

5(3)

AUTHORS:

Nikitina, V. I., Pudovik, A. N.

TITLE:

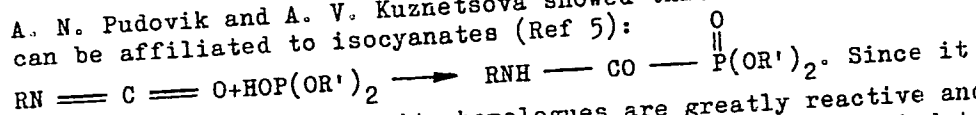
A New Method for the Synthesis of Phosphinates and Thiophosphinates (Novyy metod sinteza efirov fosfinovykh i tiofosfinovykh kislot). XXX. On the Reaction of Dialkyl Phosphorous and Dialkyl Thiophosphorous Acids With Ketene (XXX. O vzaimodeystvii dialkilfosforistykh i dialkiltiofosforistykh kislot s ketenom)

PERIODICAL:

Zhurnal obshchey khimii, 1959, Vol 29, Nr 4, pp 1219-1222 (USSR)

ABSTRACT:

A. N. Pudovik and A. V. Kuznetsova showed that the above acids can be affiliated to isocyanates (Ref 5):



Since it is known that ketene and its homologues are greatly reactive and are easily affiliated to various compounds, the authors tried to cause ketene to react as well. When carrying out the reactions of dialkyl phosphorous acids with ketene they found that these reactions require a catalyst, and that it is necessary to add to the reaction mixture a small quantity of pyridine or sulfuric acid in order to initiate the reaction. During the transformation of ketene with dimethyl-, diethyl-, dibutyl-, and di-isobutyl

Card 1/3

A New Method for the Synthesis of Phosphinates and Thiophosphinates. XXX. On the  
Reaction of Dialkyl Phosphorous and Dialkyl Thiophosphorous Acids With  
Ketene SOV/79-29-4-38/77

phosphorous acids two products form in either case: dialkyl acetophosphinates, and products of their further transformation with ketene (Scheme 2). Generally the quantity of both products is 75-80%; the acetophosphinate yield is only a fraction of the acetoxylvinylphosphinate yield. The structure of acetophosphinates was determined according to reference 6, that of acetoxylvinylphosphinates by means of the double bond. Formaldehyde results from the ozonation of the acetate of dimethyloxyvinylphosphinate. The second stage of the reaction was carried out separately. By the transformation of ethylacetophosphinate with ketene in the presence of pyridine the diethylacetoxylvinylphosphinate was obtained. The data obtained, as well as those obtained by the analyses and molecular refraction, prove the structure of the acetates of oxyvinylphosphinates. The constants of acetophosphinates and acetovinylphosphinates are contained in the table (Products 1-8). The reactions of ketene with dialkylthiophosphorous acids take place in a similar way, but the acetoxylvinylthiophosphinate yields are smaller in these reactions than in those mentioned

Card 2/3

5(3)

AUTHORS: Pudovik, A. N., Sitdikova, F. N. SOV/20-125-4-38/74

TITLE: Addition of the Incomplete Esters of Phosphoric Acids to Nitroisoamylene and Ethyl-vinylsulfone (Prisoyedineniye nepolnykh efirov kislota fosfora k nitroizoamilenu i etilvinilsul'fonu)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 4, pp 826-828 (USSR)

ABSTRACT: The authors continue their work (Ref) in the field of the addition of esters of various phosphorus containing acids etc to other compounds. It was of interest to extend the field of application of the mentioned reactions to the unsaturated nitro compounds and unsaturated nitrosulfones. This would facilitate a simple and convenient method of synthesis of nitrophosphinic- and sulfophosphinic esters which normally is either difficult or impossible (Refs 2-4). The catalysts were alcoholates of alkali metals without solvent. It was very easy to add dimethyl- and diethyl phosphoric acid to nitroisoamylene. In this connection a considerable amount of heat was produced. The reaction products are weakly smelling distillable liquids of a slightly yellow color. The addition of the ethyl ester of phosphonoacetic acid to nitroisoamylene

Card 1/3



SOV/20-125-4-38/74

## Addition of the Incomplete Esters of Phosphoric Acids to Nitroisoamylene and Ethyl-vinylsulfone

is more difficult. It requires considerable amounts of alcoholate and temperatures of 100-110° during several hours. A rather long induction period precedes the reaction. Table 1 shows the constants of the products obtained. Nitroisoamylene polymerizes only weakly in this connection. The experiments dealing with the addition of diethyl- and dimethyl thiophosphorus acid to furyl nitroethylene and  $\omega$ -nitrostyrene in the presence of alcoholates of alkali metals as well as in the presence of organic bases, further the carrying out of the reaction in solutions in all cases led to a more rapid polymerization than it was the case with the addition reaction, in spite of the use of catalysts milder (piperidine and triethylamine) than alcoholates. It was not possible to isolate the addition products, and after a several hours heating at 80-90° only the initial products were isolated. It is well-known that certain nucleophilic reagents easily add to the double bond of unsaturated sulfones, in which connection various derivatives of saturated sulfones form. The addition products are distillable liquids or crystalline colorless substances, with a weak smell (Table 2). The reactions described

Card 2/3

SOV/20-125-4-38/74

Addition of the Incomplete Esters of Phosphoric Acids to Nitroisoamylene and Ethyl-vinylsulfone

in the present paper were carried out according to the method of reference 1. The reagents were used in equimolar amounts (1/20 - 1/30 mole). Thus, it was proved that the dialkyl phosphorous- and dialkyl thiophosphorous acids as well as the acid esters of alkylphosphinic acids in the presence of an alkali catalyst are capable of adding to the double bond of the  $\alpha$ -unsaturated nitro compounds and sulfones. There are 2 tables and 4 references, 3 of which are Soviet.

ASSOCIATION: Kazanskiy gosudarstvennyy universitet im. V. I. Ul'yanova-Lenina  
(Kazan' State University imeni V. I. Ul'yanov-Lenin)

PRESENTED: December 19, 1958, by B. A. Arbuzov, Academician

SUBMITTED: November 28, 1958

Card 3/3

S/079/60/030/007/014/020  
B001/B067

AUTHORS: Pudovik, A. N., Konovalova, I. V.

TITLE: A New Method of Synthesizing the Esters of Phosphinic and Thiophosphinic Acid. XXXIV. Addition of Dialkyl Thiophosphorous Acids and Acid Esters of Ethyl- and Phenyl Phosphinic Acid to Unsaturated Hydrocarbons

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol. 30, No. 7,  
pp. 2348 - 2352

TEXT: In continuation of their earlier paper (Ref. 1) the authors studied the addition reactions of dialkyl thiophosphorous acids and acid esters of alkyl- and aryl phosphinic acids. They proceeded from diethyl-, di-n-propyl-, diisopropyl-, di-n-butyl thiophosphorous acid, from methyl-, ethyl-, butyl ester of ethyl phosphinic acid, and from methyl-, ethyl ester of phenyl phosphinic acid. The addition was made to hydrocarbons of the aliphatic series, from heptene-1 to undecene-1, and to cyclohexene. The reactions took place under irradiation of the reaction mixtures with a mercury-quartz lamp or under heating in the presence of

Card. 1/3

A New Method of Synthesizing the Esters of Phosphinic and Thiophosphinic Acid. XXXIV. Addition of Dialkyl Thiophosphorous Acids and Acid Esters of Ethyl- and Phenyl Phosphinic Acid to Unsaturated Hydrocarbons S/079/60/030/007/014/020 B001/B067

benzoyl peroxide. In both cases, the same alkyl thiophosphinates, dialkyl phosphinates, and the esters of alkyl-phenyl phosphinic acids were obtained with yields of 40-65%. A scheme of the reaction course is given. The reactions (1-3) show the initiation process and the growth of the chain, as well as the formation of the addition product. Reaction (4) causes the formation of the polymer residue at the expense of further telomerization. At an equivalent ratio of the initial reagents the polymeric residue is formed in a quantity of 10-15% of the addition product. It was shown that the dialkyl thiophosphorous acids and the acid esters of phosphinic acids add to olefins even without catalysts; a prolonged heating at 135-140° is sufficient. The addition products which were obtained by irradiation on the one hand and by the presence of benzoyl peroxide on the other are identical. The reaction rate in the case of cyclohexene was characterized by a change in concentration of the acid in the reaction mixture. It was shown that with increasing radical the phosphinate yield is gradually and slowly reduced (Fig. 1).

Card 2/3

A New Method of Synthesizing the Esters of Phosphinic and Thiophosphinic Acid. XXXIV. S/079/60/030/007/014/020  
Addition of Dialkyl Thiophosphorous Acids and B001/B067  
Acid Esters of Ethyl- and Phenyl Phosphinic Acid to Unsaturated  
Hydrocarbons

The alkyl thiophosphinates, dialkyl phosphinates, and alkyl-phenyl phosphinates are characterized in Tables 1 and 2. The acids obtained from them by saponification are given in Table 3. On the basis of the experimental results the authors arrived at the conclusion that the addition of dialkyl thiophosphorous acids to olefins in both cases does not proceed according to the Markovnikov rule but to the radical mechanism (Scheme 2). There are 2 figures, 3 tables, and 2 Soviet references.

ASSOCIATION: Kazanskiy gosudarstvennyy universitet (Kazan' State University)

SUBMITTED: July 6, 1959

Card 3/3

PUDOVIK, A.N.; MURATOVA, A.A.; KONNOVA, T.I.; FEOKTISTOVA, T.; LEVKOVA,  
L.N.

Reactions of esters of alkyl phosphonic acids with halogen-  
containing compounds. Zhur.ob.khim. 30 no.8:2624-2630 Ag  
'60. (MIRA 13:8)

1. Kazanskiy gosudarstvennyy universitet.  
(Phosphonic acid)

PUDOVYI, A.N.; KONOVALOVA, I.V.

New method of synthesizing esters of phosphinic and thiophosphinic acids. Part 35: Addition of phosphorus pentochloride to diene hydrocarbons and of partial esters of phosphorus acids to butadiene-phosphinic esters. Zhur.ob.khim. 31 no.4:1693-1699 My '61.  
(MIRA 14:5)

1. Kazanskiy gosudarstvennyy universitet.  
(Phosphinic acid)

PUDOVIK, A.N.; ALADZHEVA, I.M.

Esters of ethyleneglycoldiphosphorous acid. Zhur.ob.khim. 31 no.6:  
2052-2057 Je '61. (MIRA 14:6)

1. Kazanskiy gosudarstvennyy universitet.  
(Phosphorous acid)



PUDOVIK, A.N.; MEDVEDEVA, G.P.; KOCHETKOVA, V.I.

Reactions of phosphorous acid cyclic esters with  $\alpha$ -halo ketones.  
Zhur.ob.khim. 31 no.8:2650-2656 Ag '61. (MIRA 14:8)

1. Kazanskiy gosudarstvennyy universitet.  
(Phosphorous acid) (Ketones)

25367

S/079/61/031/008/005/009  
D215/D304

158150

AUTHORS: Pudovik, A.N., Konovalova, I.V., and Durova, O.S.

TITLE: A new synthesis method of phosphinic and thiophosphinic acids and esters. XXXIII. Synthesis of unsaturated phosphonic and thiophosphonic acids esters

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 8, 1961, 2656-2661

TEXT: This study is a continuation of previous investigations, in which it was found that derivatives of unsaturated acids of phosphorus can be obtained by adding to their incomplete esters acetylene compounds, activated with some electron repellent groups in presence of an alkaline catalyst. In this work it is shown that this method may be applied to acetylene compounds directly in conditions stimulating the mechanism of free radicals chain addition. As incomplete esters of phosphorus acids, the following compounds were used: dimethyl and diethyl-phosphorous acid esters, diethyl and di-isopropylthiophosphorous acid esters, and ethyl and isopropyl ethyl phosphonic acid esters. The addition of these

Card 1/5

25367

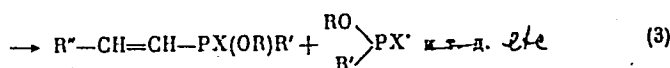
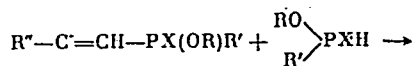
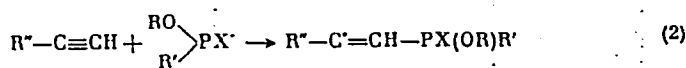
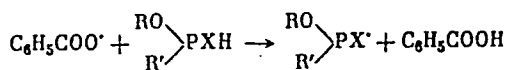
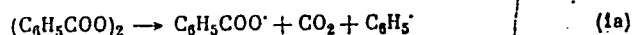
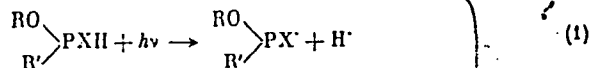
S/079/61/031/008/005/009  
D215/D304

A new synthesis method ...

esters to heptyne-1 and octyne-1 was carried out by irradiating the reaction mixture with ultra-violet light or in presence of benzoylperoxide. The chain reaction is illustrated by the following reactions.

(1), (1a), (2) and (3) correspond to initiation chain-growing and the formation of the addition product; N(4) - formation of the polymerization product. In both synthesis reactions (irradiation or benzoylperoxide), the same products - esters of alkenyl phosphoric or alkenylthiophosphonic acids were obtained,

Card 2/5



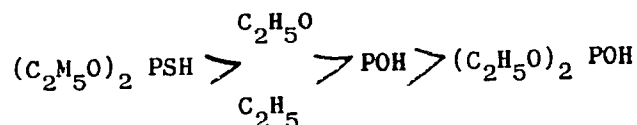
25367

S/079/61/031/008/005/009  
D215/D304

A new synthesis method...

[Abstractor's note: British nomenclature of phosphorus organic compounds is used: "onic" for quinquivalent and "inic" for tervalent P] with a yield of 25-50%, the esters being mobile, colorless liquids, sparingly soluble in water, highly soluble in organic solvents. Their characteristics are given in tabulated form. The structure of addition products was proved by the oxidation of the diethyl ester of hephenylthiophosphonic acid with  $\text{KMnO}_4$ , when n - caproic acid was obtained.

The authors investigated the addition reaction velocity of heptyne-1 to acidic ethylesters of phosphorous, thiophosphorous and ethylphosphinic acids; they found that the velocity of reaction decreased in the following series:



The obtained results prove that the investigated reactions take place through free radicals chain mechanism and against Markownikoff's rule

Card 3/5

25367

S/079/61/031/008/005/009  
D215/D304

A new synthesis method...

[Abstractor's note: His name is written thus in technical literature].  
The velocity of addition reactions of the above-mentioned esters with heptane-1, heptyne-1 and phenylacetylene decreases as follows: heptane-1 heptyne-1 phenyl-acetylene. The velocity of reactions are given graphically. It is seen that the velocity of reaction with benzoylperoxide is quite similar to that which is carried out by irradiation and that the addition reaction with phenylacetylene is much slower than others. The yield of the last reaction was very low, due to the resinification of reagents. The obtained product: diethylester of  $\beta$ -phenylvinylthiophosphonic acid was described by previous investigators, but its constants given by them differ from those found by the authors; the previously published constants were erroneous because MR based on the given data is markedly different from the calculated one. The authors carried out the synthesis of di-phosphonic derivatives by adding di-ethylphosphorous and di-ethylthiophosphorous acids to the diethylester of heptenylthiophosphonic acid, in the presence of sodium ethoxide, the reaction being an ionic one. The reaction products are thick, colorless liquids,

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S/079/61/031/008/005/009  
D215/D304

A new synthesis method...

almost insoluble in water, soluble in organic solvents. There are 1 table, 2 figures and 18 references: 14 Soviet-bloc and 4 non-Soviet-bloc. The references to the 4 most recent English-language publications read as follows: U.S.A. Patents AN 2611784, 2622096, Ch.A. 47, 9355, 9344 (1953); C.S. Marvel, T.C. Wright, Y. Polym, Sci. 8, 255 (1952); K. Leedman, R.N. Haszeldine, Y. Chem. Soc. 1634, (1954); T. Heilbron, E.R. Jones, H. Bander, L.C. Gross, Y. Chem. Soc. 604, (1949).

ASSOCIATION: Kazanskiy gosudarstvennyy universitet (Kazan State University)

SUBMITTED: July 25, 1960

Card 5/5

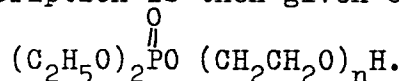
S/09/61/031/012/006/011  
D258/D301

AUTHORS: Pudovik, A. N., and Moshkina, T. M.

TITLE: Polyethylene glycols and some of their derivatives

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 12, 1961, 4028-4033

TEXT: The authors synthesized several polyethylene glycols of the general formula  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$  and the esterification products of these with either one or two molecules of  $(\text{C}_2\text{H}_5\text{O})_2\text{POCl}$  and  $\text{ClCH}_2\text{COCl}$  (separately). The products were assumed to be useful as plasticizers in producing materials for motion pictures, as surfactants and as tanning agents. The molecular weights of the lower glycols were determined by cryoscopy. The glycols are soluble in alcohol, benzene, dioxane and water; their solubility in ether decreases with increasing molecular weight. A description is then given of the preparation of monophosphate esters



Card 1/2

Polyethylene glycols and ...

S/079/61/031/012/006/011  
D258/D301

The principal characteristics of the synthesized polyethylene glycols (I) and their monophosphates (II), diphosphates (III), monochloroacetates (IV) and dichloroacetates (V) are given in tabulated form. There are 1 figure, 3 tables and 3 references: 1 Soviet-bloc and 2 non-Soviet-bloc. The reference to the English-language publication reads as follows: R. Forgyce, H. Lovell and H. Hibbert, J. Am. Chem. Soc., 61, 1905, (1939).

ASSOCIATION: Kazanskiy filial nauchno-isslyedovatel'skogo kino-fotoinstituta (Kazan Branch of the Scientific Research Moving Picture Photography Institute)

SUBMITTED: December 26, 1960

Card 2/2



S 3630

31195  
S/079/61/031/012/009/011  
D204/D301

AUTHORS: Pudovik, A. N., and Krupnov, G. P.

TITLE: A new method of synthesizing phosphinic and thiophosphinic esters. XXXVI. Synthesis of phosphinic acid derivatives containing cyclic radicals in the ester group

PERIODICAL: Zhurnal obshchey khimii, v. 31, no. 12, 1961, 4053-4055

TEXT: Compounds of the general formulae  $(RO)_2 \overset{O}{\underset{|}{P}} CH_2 CH(R')X$  (I), where  $R = C_6H_{11}^-$ ,  $C_6H_5CH_2^-$ ,  $R' = -H$ ,  $-CH_3$ ,  $X = -CN$ ,  $-COOCH_3$ ,  $-COOC_4H_9$  and  $(RO)_2 \overset{O}{\underset{|}{P}} CH(C_6H_5)NHC_6H_4X$  (II), where  $R = C_6H_{11}^-$ ,  $C_6H_5^-$ ,  $C_6H_5CH_2^-$ ,  $X = p - CH_3$ ,  $-H$ ,  $p - NO_2$  were prepared in a search for new plasticizers for cellulose esters and other polymers. The ge-  
Card 1/3

31195

S/079/61/031/012/009/011

D204/D301

A new method of synthesizing ...

neral method of preparation consisted of adding esters of dicyclohexyl, dibenzyl and diphenyl phosphorous acids to unsaturated, electrophilic compounds, in the presence of a catalyst. Na alcoholate in absolute alcohol was added dropwise to an equimolecular mixture of the appropriate phosphorous ester and either an ester or nitrile of an unsaturated carboxylic acid or a Schiff's base, with constant stirring, keeping the temperature below 50-90°C. The reaction mixture was then heated for 1 - 2 hours on a steam bath. The products were purified either by distillation (ordinary or high-vacuum), or by repeated washing with water to remove the catalyst, and drying. The yields were 13.6 - 68% in the case of (I) and 61 - 88% in the case of (II). Distillation of the reaction products was difficult owing to a tendency towards charring and decomposition, but comparable purity could be achieved by the washing method. Esters (I) were colorless, involatile liquids insoluble in water but soluble in a number of organic solvents; aminophosphinic esters (II) were crystalline substances, insoluble in water but soluble in alcohol. Physical constants of both types of products are tabulated. There are 2 tables and 3 references: 2 Soviet-bloc

Card 2/3

31195

S/079/61/031/012/009/011  
D204/D301

A new method of synthesizing ...

and 1 non-Soviet-bloc. The reference to the English-language publication reads as follows: Atherton, Koward and A. Todd, J. Chem. Soc. (1948), 1182.

ASSOCIATION: Kazanskiy filial vsesoyuznogo nauchno-issledovatel'skogo kinofotoinstituta (Kazan Branch of the All-Union Scientific Research Institute of Motion Picture Photography)

SUBMITTED: December 26, 1960

X

Card 3/3

29016

S/020/61/140/004/017/023  
B106/B110

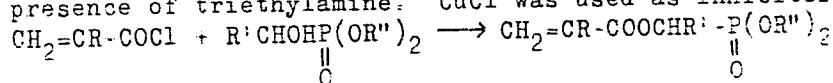
15 815D

AUTHORS: Pudovik, A. N., Kashevarova, E. I., and Rudnev, Yu. P.

TITLE: Phosphorus-containing acrylic and methacrylic esters

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 140, no. 4, 1961, 841-843

TEXT: Polymers and copolymers of acrylic and methacrylic esters containing sulfur, fluorine, tin, lead, silicon, mercury, etc. often have particular properties: high hardness and heat resistance, good adhesion to glass and metal, low permeability to X-rays, low combustibility, etc. In this connection, a method was developed for the synthesis of acrylic and methacrylic esters containing phosphorus in the alcohol component. Some properties of these esters were studied. The synthesis is based on the reaction of acid chlorides of acrylic and methacrylic acids with hydroxy-alkyl phosphinic esters (molar ratio 1 : 1) in ether solution in the presence of triethylamine. CuCl was used as inhibitor.



Card 1/6

29016

S/O20/61/140/004/C17/023

B:06/B:10

Phosphorus-containing acrylic ...

(R = H or CH<sub>3</sub>; R' = H or CH<sub>3</sub>; R'' = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub> . ) Reactions proceed smoothly in most cases, esters form with yields of 60-70%. The α-hydroxy-alkyl phosphinic esters used as initial substances were prepared by reacting formaldehyde and acetaldehyde with dialkyl phosphorous acids in the presence of sodium alcoholate, acryl and methacryl chlorides were obtained from acids by reaction with phosphorus trichloride. The characteristics of the acrylic and methacrylic esters synthesized are shown in Table 1. All these compounds are easily soluble in methanol, ethanol, ether, acetone, benzene, and carbon tetrachloride. Moreover, esters containing methyl and ethyl radicals in the phosphono group are soluble in water. When the α-(dimethyl phosphono)-ethyl methacrylic ester is polymerized in the presence of 0.3 mole% benzoyl peroxide (9 hr at 80°C), a solid transparent polymer formed which swelled strongly in water, alcohol, benzene, acetone, and carbon tetrachloride. The polymer burns with sooty flame, but does not keep burning by itself. The polymer obtained by polymerization of α-(diethyl phosphono)-ethyl methacrylic ester in the presence of 0.5 mole% benzoyl peroxide (30 hr at 100°C) is a soft, transparent, plastic mass readily soluble in methanol, ethanol, and acetone. It is precipitated by petroleum ether from solutions in benzene.

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29016

S/020/61/140/004/017/023

B106/B110

Phosphorus-containing acrylic

and acetone. Methyl methacrylate and  $\alpha$ -(dimethyl phosphono)-ethyl methacrylic ester (weight ratio 83 : 17) were copolymerized at 75°C for 1.5 hr. The copolymer obtained is a transparent and solid product soluble in acetone and benzene. A white, solid, nontransparent product containing 2.2% phosphorus was obtained after reprecipitating by dissolution in acetone precipitating with petroleum ether, and subsequent drying in vacuo. This copolymer burns with sooty flame and keeps burning when the flame has been removed. There are 1 table and 16 references: 11 Soviet and 5 non-Soviet. The three most recent references to English-language publications read as follows: G. Sumrell, I. Briskin, G. Ham, C. S. Shramm, J. Am. Chem. Soc., 81, 4308 (1959); C. S. Marvell, W. S. Anderson, Ind. and Eng. Chem., 47, 344 (1955); A. Saiton, E. Rochow, J. Org. Chem., 23, 116 (1958).

ASSOCIATION: Kazanskiy gosudarstvennyy universitet im. V. I. Ul'yanova-Lenina (Kazan' State University imeni V. I. Ul'yanov-Lenin)

PRESENTED: May 8, 1961, by B. A. Arbuzov, Academician

SUBMITTED May 5, 1961

Card 3/65

PUDOVIK, A.N.; MOSHKINA, T.M.

Polyethylene glycols and some of their derivatives. Zhur.  
ob.khim. 31 no.12:4028-4033 D '61. (MIRA 15:2)

1. Kazanskiy filial Nauchno-issledovatel'skogo kinofotoinstituta.  
(Glycols)

PUDOVIK, A.N.; KRUPNOV, G.P.

New method of synthesizing esters of phosphinic and thiophosphinic acids. Part 36: Synthesis of the derivatives of phosphinic acids with cyclic radicals in ester groups. Zhur. ob.khim. 31 no.12:4053-4055 D '61. (MIRA 15:2)

1. Kazanskiy filial Vsesoyuznogo nauchno-issledovatel'skogo kinofotoinstituta.

(Phosphinic acid)

(Phosphinitic acid)



PUDOVIK, A.N., KUZNETSOV, YE.V., MALICHENKO, B.F., GRISHINA, O.P.

The synthesis of various phosphorus-containing monomers.

Report presented at the 12th Conference on high molecular weight compounds,  
devoted to monomers, Baku, 3-7 April 62

PUDOVIK, A.N.; FAYZULLIN, E.M.

Reactions of phosphorus acid chlorides with glycerol epichlorohydrin  
and glycidol ethers. Zhur. ob. khim. 32 no.1:231-237 Ja '62.

(MIRA 15:2)

1. Kazanskiy gosudarstvennyy universitet.

(Phosphorus acids) (Glycerol) (Ether)

PUDOVIK, A.N.; KONOVALOVA, I.V.; ISHMAYEVA, E.A.

New method of synthesizing phosphinic and thiophosphinic acid esters.  
Part 37: Addition of nucleophilic reagents to butadiene- and  
methylbutadienephosphinic esters. Zhur. ob. khim. 32 no.1:237-241  
Ja '62. (MIRA 15:2)

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(Phosphinic acid)

PUDOVIK, A.N.; KONOVALOVA, I.V.

Reactions of vinyl acetate with partial esters of phosphorus  
acids. Zhur.ob.khim. 32 no.2:467-471 F '62. (MIRA 15:2)  
(Vinyl acetate)  
(Phosphorus acids)